ABSTRACT OF THESIS

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Title of Thesis Reactions of alkyl radicals

The field of alkyl radicals reactions has been reviewed and tables have been drawn up which include the most reliable values of rate constants, rate constant ratios, Arrhenius parameters etc. for combination of like and unlike radicals; disproportionation reactions; metathetical reactions; addition to multiple bonds and decomposition of alkyl radicals.

The addition of methyl, ethyl, isopropyl and t-butyl radicals to acetylene has been studied in systems in which acetaldehyde, propionaldehyde, isobutyraldehyde or trimethylacetaldehyde have been photolysed in the presence of acetylene.

The kinetic apparatus constituted a high vacuum static system of conventional design. The different products from the reactions have been analysed on a Gas Chromatography apparatus with a column of activated alumina poisoned with 1% of squalane. The A factors and activation energies deduced from the results for the different addition reactions are

Radical	log A ($mole^{-1}$ cm^3 sec^{-1})	E ($Kcal$ $mole^{-1}$)
Me	11.4	7.7
Et	11.0	7.0
Pr^i	11.2	6.9
Bu^t	10.7	5.4

Isomerization of the alkenyl radical formed when isopropyl or t-butyl radicals add to acetylene have been observed and its pressure dependance studied. A mechanism which accounts for the isomerization products has been postulated.

Use other side if necessary.

Photolyses of di-t-butyl ketone and pivalaldehyde have yielded information on the ratio of rate constants of disproportionation and combination of t-butyl radicals. The value found in the experiments was

$$\Delta(Bu^t, Bu^t) = 3.19$$

Information on cross-disproportionation and cross-combination of t-butyl radicals with ethyl and isopropyl at a temperature of 80°C has been gathered from the results of photolyses of mixtures of the corresponding di-alkyl-ketones. Values deduced from the results of the runs are

$$\Delta(Et, Bu^t) = 0.48$$

$$\Delta(Pr^i, Bu) = 0.70$$

$$\Delta(Bu^t, Et) = 0.31$$

$$\Delta(Bu^t, Pr^i) = 0.67$$

The rate constants for the combination of t-butyl radicals with ethyl and isopropyl are twice the geometric means of the rate constants for the corresponding autocombinations.

REACTIONS OF ALKYL RADICALS

by

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A mi madre

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TABLE OF NOMENCLATURE

A	=	A factor } Arrhenius parameters
E	=	Activation energy } Arrhenius parameters
$D(Y - Z)$	=	Bond dissociation energy of the bond Y - Z
ΔH (1)	=	Heat of reaction (1)
ΔH_f° (X)	=	Heat of formation of substance X
k_1	=	Rate constant of reaction (1)
Me	=	Methyl Radical
R_X	=	Rate of formation of product X
R_X (1)	=	Rate of formation of X by reaction (1)
R	=	Alkyl Radical
R	=	Gas constant
ΔS_1	=	Entropy change of reaction (1)
T	=	Absolute temperature
[X]	=	Concentration of X

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CHAPTER I

REACTIONS OF ALKYL RADICALS

Although the existence of free radicals was suggested many years ago, it was not until recently that the availability of refined analytical techniques such as low temperature distillation and mass spectrometry made possible a quantitative study of their reactions. The advent of gas chromatography in 1955 made possible the analysis of a complex mixture of hydrocarbons and since then many results for different types of radical reactions have been reported.

In the present chapter the field of the alkyl radicals is summarily presented.

1.1 THE PRODUCTION OF ALKYL RADICALS. The simplest way of getting a radical consists of breaking the appropriate bond in a molecule that contains it. This can be done in a variety of ways, and the ideal source would be one which would produce the clean radical thermally equilibrated with its environment. Unfortunately this is not always achieved. Molecules often split up into two or more active species that complicate the system. Hot radicals, that is to say, not in thermal equilibrium with their surroundings are produced and this introduces a further complication in the study of their reactions.

Two main methods have been used in the past to produce alkyl radicals. One consists of splitting up a molecule to give the desired radical. The indirect method consists of producing an unstable molecule or radical that would decompose to yield the radical.

a) Primary sources of alkyl radicals.

The pyrolysis of molecules has been studied in the gas phase. As radical sources they have the disadvantage of having quite a high temperature coefficient of decomposition which restricts the temperature range over which they may most conveniently be used.

Di-t-butyl peroxide is an excellent thermal source of methyl radicals in the temperature range 125-180°C [1] and the mechanism of its decomposition is well established.

Azomethane has been used as a source of methyl radicals at 250-300°C, and the mechanism of its thermal decomposition is well understood [2]. Other compounds have also been studied [3]. They cannot however compete as sources of radicals with the corresponding photolytic sources.

The pyrolyses of metal alkyls such as mercury dimethyl can be used as sources of radicals at higher temperatures [4-8].

Alkyl iodides have been used as thermal sources of radicals. The presence of mercury vapour in the system partially prevents the iodine atoms from recombining with the newly formed radicals [9].

Photochemical sources of alkyl radicals. The advantage of light as a means of producing radicals is that it is easy to control their rate of production by simply varying the light intensity. Further, a homogeneous concentration of radicals throughout the reaction volume is desired for most calculations and this is best achieved with photolytic sources.

Metal alkyls have been succesfully photolysed in the gas phase as sources

of radicals [10]. Both dimethyl and diethyl mercury have been used. The higher metal alkyls are less volatile and thermally unstable. The mechanism of their photolysis appears to be complicated by heterogeneous thermal reactions. Evidence has been found of the existence of "hot" radicals in the system.

Azomethane, azoethane, azo-n-propane and azo-iso-propane have been photolysed and the mechanism of their decomposition seems well understood [11,12, 109] Azo-n-alkanes are clean sources of the corresponding n-alkyl radicals and should prove good sources for the study of some of their most interesting reactions.

Di-t-butyl peroxide has also been used as a photolytic source of alkyl radicals [13], and some values for cross-disproportionation ratios have been deduced from the results of the runs. It has however no general applicability.

The photolysis of ketones is a more satisfactory method. The mechanism by which the lower ketones decompose is well established [14,15]. Many of the metathetical reactions of methyl radical have been studied using acetone as the source of radicals [16]. Diethyl ketone is also a most useful source of ethyl radicals.

Higher ketones do not photolyse so cleanly. Nicholson [17] has photolysed methyl n-propyl ketone, methyl iso-propyl ketone, methyl n-butyl ketone and methyl n-amyl ketone and found that only in the case of methyl iso-propyl ketone the expected alkyl radicals are cleanly produced. In all other cases an intramolecular rearrangement takes place and an olefin and smaller ketone is formed, along with the corresponding alkyl radicals. This confirms previous work on methyl n-butyl ketone [18].

Methyl isopropyl ketone and methyl t-butyl ketone have been recently photo-

lysed in the presence of acetone [19] for the study of the low temperature reactions of methyl with isopropyl and t-butyl radicals. From the table of results it can be deduced that both ketones are clean photolytic sources of the corresponding radicals.

Mason has photolysed di-n-propyl ketone [20] and found that ethylene and methyl n-propyl ketone, as well as n-propyl radicals are formed in the primary photolytic act.

The photolysis of diisopropyl ketone [21] seems a good source of isopropyl radicals without complicating intramolecular rearrangements.

Kraus and Calvert have photolysed di-t-butyl ketone, diisobutyl ketone and disec-butyl ketone [22]. Di-t-butyl ketone has proved a useful source of t-butyl radicals, producing only CO and two t-butyl radicals in the primary act. The photolysis of diisobutyl ketone and disec-butyl ketone appears complicated with the formation of considerable amounts of olefin and smaller ketones in the primary photolytic act, as well as the corresponding radical.

This intermolecular rearrangement observed, seems to be general to all ketones containing hydrogen atoms in position respect to the CO group. Photolysis of aldehydes having an alkyl group with at least three carbon atoms in a straight chain together with the carbonyl group also yield products which suggest the existance of the same type of rearrangement.

Presenting results for the photolysis of several ketones and aldehydes, Pitts [23] has concluded that the rearrangement takes place through the formation of an activated six-membered ring, although the possibility of a hydrogen

shift from γ to α position was not ruled out. More recently Borrell [24] has shown how the problem seems general to all carbonyl compounds and has been observed in pyrolyses, photolyses, electron impact and radiolyses in both liquid and gas phase.

Photodecomposition of, say, methyl n-propyl ketone takes place via the following reactions:

$$CH_3CO\,C_3H_7 + h\nu \longrightarrow C_8H_7CO + CH_3 \qquad 1$$

$$\longrightarrow C_2H_4 + CH_3COCH_3 \qquad 2$$

Reaction 1 is a scision of the bond adjacent to the carbonyl group forming free radicals and is common to all ketones. Reaction 2 is a direct intramolecular rearrangement into molecular products and is confined to the higher members of the series. They are named "Norrish type I" and "Norrish type II" reactions. When reactions of this type take place in solution, or in the presence of a free radical scavenger, type I reaction is suppressed, while type II is not affected. It has also been proved to be independent of temperature.

The type II split is not only limited to aldehydes or ketones but is also present in acids and esters. The group in position α to the carbonyl group has little effect on the reaction. It is also evident that the reaction is independent of the β group: photolysis of acetic anhydride will yield acetic acid and ketone by a type II reaction [159]. If any carbonyl compound not containing hydrogen atoms in position γ is photolized, type II reaction does not take place.

Pyrolysis of many carbonyl compounds have shown the existance of an entirely

similar mechanism. Ketones and other compounds that form an olefin and a lower member of the series have not been fully studied because the products also decompose. In pyrolysis the type II reaction is the low temperature form of decomposition while type I, which forms free radicals is important only at higher temperatures.

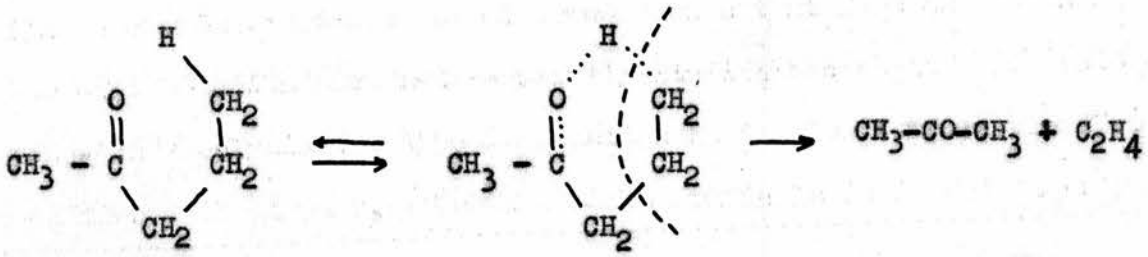
Mass spectrometric studies of aliphatic ketones have shown the formation of a group by scision of the β bond to the carbonyl group to form a charged lower ketone. Methyl n-propyl ketone and higher methyl alkyl ketones show a peak at mass 58 which is no present if the alkyl group of the ketone has not hydrogen atoms in γ position. The same effect was found in ethyl alkyl ketones and isopropyl alkyl ketones having hydrogen atoms in that position.

Similar effects were observed with carboxylic acids having hydrogen atoms attached in the γ position. When carbon-13 was substituted into the carbonyl group the peak moved from mass 60 to mass 61, thus proving that the carbonyl group was present in the ion.

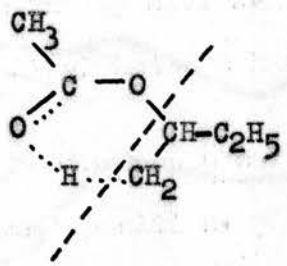
The effect is also observed in aldehydes and esters.

Evidence, for a type II reaction was also found in radiolysis of some ketones.

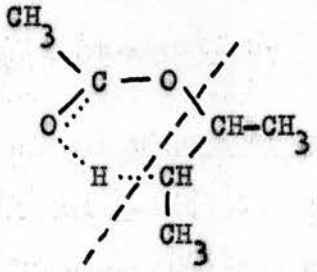
For this reaction to take place in such a variety of conditions there must be a form of decomposition common to all large carbonyl compounds in a specific manner. As the reaction is independent of the α and β groups the most probable mechanism involves the formation of a six-membered ring, followed by split to molecular products. The enolic form of the ketones is indeed known [160].



The cyclic intermediate explains the minimum size of the molecules required for the reaction. The argument finds sopport on the work of Haag and Pines on the pyrolysis of 2-butyl acetate [161]. There are two possible intermediates shown below



I



II

In the case of I three hydrogen atoms are available, while there are only two in the intermediate II. The ratio of butene-1 to butene-2 should be 3:2 as in fact is found.

Perfluoroalkyl radicals have also been produced from the photolysis of the corresponding ketones. The radicals are cleanly produced by a very simple mechanism of decomposition.

Diethyl ketone, diisopropyl ketone and di-t-butyl ketone have been used in the work presented here to study the low temperature reactions between radicals in the systems ethyl/t-butyl and isopropyl/t-butyl.

Aliphatic aldehydes. The photolysis of acetaldehyde has been much investigated [25]. Although the mechanism of its decomposition is not simple and stable products are produced in the photolytic act, methyl radicals are also formed.

Information on higher aldehydes does also exist [26-30]. Photolysis of the aldehyde RCHO follows the reaction scheme below

$$RCHO + h\nu \longrightarrow R + CHO \quad (a)$$
$$\longrightarrow RH + CO \quad (b)$$
$$\longrightarrow r + H_2CO \quad (c)$$
$$\longrightarrow r' + CH_3CHO \quad (d)$$
$$\longrightarrow r' + CH_3 + CHO \quad (e)$$
$$\longrightarrow CH_3 + r'CHO \quad (f)$$

Process (a) is the only yielding the radical R. Processes (a) and (b) take place in approximately equal amounts. Process (c) has been observed in the photolysis of propionaldehyde; it amounts to about 2.5% of the total CO produced. Process (d) is the Norrish type II reaction and can amount to as much as 60% as in the case of isovaleraldehyde [30]. r and r' are olefins, which are also products of disproportionation and decomposition of the radicals. Reaction (f) does not amount to more than 10% and often is of the order of 2%.

It can be seen from the above scheme that aliphatic aldehydes are not good primary sources of radicals. Their use as secondary sources will be discussed later.

b) Secondary sources of alkyl radicals.

The mercury photosensitized decomposition of paraffins has been used as a source of alkyl radicals and some information on their reactions has been ga-

thered from the results [31-33]. The inconvenience of the method lies in the fact that some of the most interesting reactions of the radicals produce the same paraffin which originated them, and its determination is thus imposible. Besides, more than one radical is often formed although secondary and terciary alkyl radicals are preferably produced.

The mercury photosensitised addition of hydrogen atoms to olefins suffers the same disadvantages as mentioned in the case of mercury photosensitized decomposition of paraffins. The olefin is the most interesting product of disproportionation, as the alkane can be formed in other ways. In this case however, disproportionation has to be followed by the rate of formation of paraffin. Due to the high exothermicity of addition, radicals thus produced are "hot" and it is not surprising that values of rate constants of reactions studied using this radical source do not generally agree with other determinations of the same rate constants. Addition of an inert gas to the system tends to overcome this difficulty [34]. A further difficulty lies in the fact that two isomeric radicals are always produced.

Quite recently a new methyl radical source has been found in the photosensitised decomposition of methyl mercury chloride [35]. In the primary act, methyl radicals, mercury atoms and ClHg are formed. This reaction has not yet been studied for other radicals.

The aliphatic aldehydes are not good primary sources of radicals; they are however excellent secondary sources for the study of reactions of alkyl radicals as has been shown by Gruvent and Calvert [36] and later by Birrell, Kerr, Metcalfe and Trotman-Dickenson [28,30,37-40]. Although the radical R is not cleanly produced in the photolysis of the aldehyde RCHO, the hydrogen atom in the aldehydic

group is easily removed by most radicals

$$R + RCHO \longrightarrow RH + RCO$$

by decomposition of RCO the radical R is regenerated:

$$RCO \longrightarrow R + CO$$

This sets up a chain. At a sufficiently high temperature most of the radicals do not come from the primary process but from the chains thus set up, and the fact that the photolysis is not clean becomes less and less important. The chain may also be initiated by a radical other than R [41].

Organic esters are not good primary sources of alkyl radicals [42,43]. However, organic formates have successfully been used as secondary sources of radicals in the study of some of their reactions [44,45]. The hydrogen atom of the formic group is easily removed

$$R + HCOOR' \longrightarrow RH + COOR'$$

Radical COOR' decomposes

$$R'COO \longrightarrow CO_2 + R'$$

producing a radical thermally equilibrated with its surroundings.

The reactions which alkyl radicals released into a system from any of the above sources may undergo are combination, disproportionation metathesis, addition to multiple bond, isomerization and decomposition. Some reviews on these reactions have recently appeared [46,47,48] and only a brief summary of the results

already reported in the literature will be presented here.

The experimental work presented in this thesis includes only those reactions of radicals taking place at low temperature (up to about 200°C). Discussion of results, taken in conjunction with information gathered from previous publications, will be left until the discussion section of this thesis.

1. 2 COMBINATION OF ALKYL RADICALS. When radicals R are released into a system, dimerization will take place to some extent, the rate constant being

$$k_c = \frac{R_{R_2}}{[R]^2}$$

Where R_{R_2} is the rate of formation of the compound R_2 and $[R]$ is the concentration of radicals R.

There is no difficulty in the determination of the rate of production of the dimer of any small radical in the gas phase. If few rate constants of combination of radicals are known, it is because the concentration of radicals is far lower than the limits of analytical detection, and an indirect aproach has to be used.

The most general method employed in the calculation of rate constants of combinations consists in calculating those concentrations from a knowledge of their life-times as measured by means of the rotating sector technique. Combination of life-times with rates of release of radicals in the system would give their mean concentration.

Melville and Burnett have given a full description of the method [49]. It can only be applied to systems which are well understood and with relatively few elementary reactions.

Methyl Radicals. The first determinations of the rate constant for the combination of methyl radicals [50,51,52] are not very reliable, as the mechanism of the photolysis of acetaldehyde used as a source of methyl radicals is not yet fully understood. The progress of the reaction was followed by the pressure change in a static system. Although they failed to get correct rate of abstrac-

tion of hydrogen atoms by methyl radicals, agreement with posterior determinations was good.

The first satisfactory measurement of the rate constant using the sector method was achieved by Gomer and Kistiakowsky [53] with the photolysis of acetone and mercury dimethyl. They found the rate constant for the combination of methyl radicals to be

$$k_c = 10^{13.65} \quad e^{\pm 700/RT} \quad \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

in the temperature range 125-220°C independently of radical source and at a total pressure between 10 and 50 mm Hg.

Kistiakowsky and Roberts, later restudied the photolysis of acetone [54] and corrected the earlier value to

$$k_c = 10^{13.57}\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

at 165°C and an acetone pressure of 30 mm Hg. They found the same value for the combination of trideuteromethyl radicals.

Shepp, modified the mathematical treatment of the rotating sector technique [55] to allow for both first and second order removal of radicals and recalculated those values finding

$$k_c = 10^{13.34}\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

at 125-175°C and

$$k_c = 10^{13.58}\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

at 165°C.

It seems unlikely that these values will soon be improved upon, and the value log $k_c = 13.34$ is generally accepted.

The rate of combination of radicals has also been measured by two other quite different methods of lower precision. Ingold, Lossing and Tickner [56,57] produced methyl radicals by thermal decomposition of di-t-butyl peroxide and dimethyl mercury in a flow system. Gases were directly passed through a pin hole leak in a quartz thimble into the ionization chamber of a mass spectrometer. The amounts of methyl, methane and unchanged radical source were determined for different separations between the furnace and the leak. The rate constant for the combination of methyl radicals between 850 and 975°C at a pressure of helium of 15 mm Hg and 30-50 microns of organic vapour was found to be

$$k_c = 10^{12.71} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

Using the same technique, Ingold and Lossing [58,59] found a value of

$$k_c = 10^{13.11} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

at 160°C. They also found a negative activation energy $E = -2.2 \pm 0.5$ kcal/mole They tried to explain the negative temperature coefficient from 161 to 814°C by a change of the effective collision diameters with temperature, or a change of the steric factors [60]. Both negative temperature coefficient and low values of the rate constants may be simply due to the low pressure used in the experiments [54,146].

Moseley and Robb have developed another method for the direct determination of rate constants for radical combinations in the gas phase [61]. Measurements of the pressure changes occurring in the gas when a photoinitiated reaction causes

adiabatic temperature changes, are recorded by means of a diaphragm-type manometer of a sensitivity of 10^{-4} mm Hg and a time response of less than 10^{-3} secs. Studying the mercury photosensitized decomposition of acetone at room temperature and 75 mm Hg they found a value [62]

$$k_c = 10^{13.58} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

The agreement among the three totally different methods of calculating the rate of combination of methyl radicals is excellent.

The combination of trifluoromethyl radicals has been studied by Ayscough[63] by the rotating sector technique. He found that at 127°C the rate constant was

$$k_c = 10^{13.36} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

using hexafluoroacetone as radical source.

Pritchard and Dacey by photolysing a mixture of acetone and hexafluoroacetone [64] found an activation energy for the combination of trifluoromethyl radicals of E = 2.1 kcal/mole between 30 and 170°C and supposing the activation energy for the combination of methyl radicals, and the combination of methyl with trifluoromethyl radical to be zero. They show in support of the finding that the relative A factors can be predicted in terms of the transition state theory. It must be noted however that none of the similar values for cross-combination of other radicals can be similarly predicted.

Ethyl Radicals. Ivin and Steacie have applied the rotating sector method to the study of the combination of ethyl radicals produced in the photolysis of diethyl mercury [65]. The mechanism of decomposition is relatively complica-

ted and the value deduced from their results [66] for the rate constant

$$k_c = 10^{13.3} \exp(-\ 700/RT)\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

does not seem very reliable.

The best determination of the rate constant for the combination of ethyl radicals is that deduced from studies of the photolysis of diethyl ketone with intermitent illumination, by Sheep and Kutschke [67]. They found a value

$$k_c = 10^{14.2} \exp(-2000 \pm 1000/RT)\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

at ketone pressures between 10 and 50 mm Hg and in the temperature range 50 to 150°C. Their value at 100° is in good agreement with the previous determination.

Propyl Radicals. As the radical grows in complexity, the determination of the rate of combination by the sector method becomes more difficult as the mechanism of decomposition of the radical source is less clean. The method has been applied to the study of the reaction of n-propyl radicals produced in the photolysis of di-n-propyl ketone [68]. The value

$$k_c = 10^{15.8}\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

is much higher than the corresponding values for other radicals and the authors admit that it might be high by as much as a factor of 20.

The determination of the rate of combination of isopropyl radicals by the rotating sector method has been recently carried out by Miss E. L. Metcalfe in this laboratory. Radicals were produced by the photoinitiated chain decomposition of

isobutyraldehyde and the photolysis was carried out in the presence of constant pressures of ethylene. The concentration of radicals under steady and intermittent illumination was measured from the addition reaction to the olefin. Correction for first and second order removal of radical as introduced by Sheep[55] gave a rate constant for the combination of isopropyl radicals which may be taken as

$$k_c = 10^{13.9} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

and which is independent of temperature, withing experimental error, from 81 to 169°C.

Larger Alkyl Radicals. Values for the recombination of other alkyl radicals has not yet been reported. When calculating rate constants for reactions of radicals, their concentration is generally measured in terms of the rate of formation of the dimer, and thus the rate of recombination of radicals has to be assumed. It can be seen that the experimentally determined values give an activation energy which is zero or very nearly so. A great error will then not be made if we assume the activation energy for all combinations of radicals to be zero, even that of ethyl radicals which has been found to be 2 ± 1 Kcal/mole. When more accurate work on combination of radicals be presented, the corresponding corrections can be easily made.

The experimentally found A factors lie in the vecinity of $10^{14 \pm 1}$. We may safely assume that all A factors are then $10^{14.0}$ and subsequent corrections will be easily made when actual values are available.

For the purpose of presenting values of other rate constant in this thesis, the rate constants of radical combinations will be taken as follows:

Methyl Radicals $k_c = 10^{13.34}$ mole^{-1} cm^3 sec^{-1}

Other Radicals $k_c = 10^{14.0}$ mole^{-1} cm^3 sec^{-1}

and all are assumed to be independent of temperature.

Considerations on radical combinations. When two atoms combine, the excess of energy from the formation of the chemical bond is generally sufficient to dissociate the molecule again, unless it is lost by collision with other molecules. If two complex radicals combine, the many internal degrees of freedom will take care of that energy. Marcus and Rice suggested [69,70] that there should be third body restrictions in the combination of methyl and ethyl radicals at low pressures.

Early studies on the acetone photolysis [71,72,73] showed some sort of pressure dependance but it was not until the work of Kistiakowsky and Roberts[54] that a definite fall of the rate constant for the combination of methyl radicals at low pressures was found. k_c is about one third of its value at high pressures, when the total pressure of the system is 1 mm Hg. The work of Dodd and Steacie [74] confirms this finding. They showed the effect to be due to third body restrictions by adding an inert gas to the acetone.

The corresponding pressure effect is much smaller in the case of ethyl radicals, as found by Brinton and Steacie in the photolysis of diethyl ketone at pressures down to 10^{-2} mm Hg.

Other alkyl radicals have many more internal degrees of freedom and one does not expect any pressure effect to be significant in their combination reactions.

The rate constant for the bimolecular combination of radicals as given by the transition-state theory is

$$k_c = e^2 \frac{kT}{h} e^{\Delta S_c^{\ddagger}/R} e^{-E/RT}$$

Assuming $\Delta S_c^{\ddagger}$ to be similar to ΔS_c (that is to say, the activated complex to be like the final product) then $\Delta S_c^{\ddagger}$ is about -25-30 e.u. Thus A factors of the Arrhenius expression for combinations of radicals should be of the order of 10^{11} mole^{-1} cm^3 sec^{-1}. The combination of atoms, with no rotational entropy to lose should have A factors close to the rate of collision between particles, $10^{14.3}$ mole^{-1} cm^3 sec^{-1}. As seen previously, the rates of combination of radicals approach the latter value. It has been assumed that in the activated complex the radicals rotate freely while being loosely held together, and so have no rotational entropy to lose[70]. This would explain the abnormally high A factors.

<u>The combination of unlike radicals</u>. If two different radicals are released into a system three combinations many occur

$$2A \longrightarrow A_2 \quad \ldots\ldots \quad k_{aa}$$
$$2B \longrightarrow B_2 \quad \ldots\ldots \quad k_{bb}$$
$$A + B \longrightarrow AB \quad \ldots\ldots \quad k_{ab}$$

it can be seen that

$$\frac{k_{ab}}{k_{aa}^{\frac{1}{2}} x k_{bb}^{\frac{1}{2}}} = \frac{R_{AB}}{R_{AA}^{\frac{1}{2}} x R_{BB}^{\frac{1}{2}}}$$

where R_{AA} is the rate of formation of the product A_2. The simple collision theory of chemical Kinetics predicts this ratio to be two, if none of the above reactions has an activation energy. Several measurements of the ratio have been reported, and further information may be deduced from other published results [76]. Table 1. 1 summarises some of the results for alkyl and alkoxyl radical combinations. None of them varies with temperature, which seems an indication that combination of radicals have small if any activation energy and that it occurs at every collision; the collision diameters being slightly different from those required for the calculation of transport properties.

TABLE 1.1. COMBINATION OF UNLIKE RADICALS

RADICALS A	B	$k_{ab}/k_{aa}^{\frac{1}{2}} k_{bb}^{\frac{1}{2}}$	Ref.
Methyl	trideutero methyl	1.9	77
Methyl	trifluoro methyl	1.5	78
Methyl	ethyl	1.9	79
		2.0	80
Trideutero methyl	ethyl	1.8	81
Methyl	pentafluoro ethyl	2.0	87
Methyl	n-propyl	2.6	82
		1.4	83
		2.1	17
Trideutero methyl	$CH_3CH_2CO_2$	1.8	84
Trifluoro methyl	perfluoro n-propyl	1.8	90
Methyl	isopropyl	1.9	125
Methyl	t-butyl	1.9	13
Methyl	sec-butyl	1.8	113
Methyl	n-pentyl	1.6	85
Methyl	acetyl	1.7	42
		1.7	77
		2.2	86
Trideutero methyl	CD_3CO	2.0	84
Methyl	acetonyl	1.5	88
		2.0	93
CF_2Cl	CF_2ClCF_2	2.0	89
Ethyl	n-propyl	1.9	37
Ethyl	i-propyl	2.0	38
		2.0	43
Ethyl	t-butyl	1.9	(b)
Ethyl	n-heptafluoro propyl	3.2	91
Ethyl	pentanonyl	1.7	75
		1.5	92
n-propyl	n-butyl	2.2	39
i-propyl	t-butyl	2.0	(b)

1.3 DISPROPORTIONATION OF ALKYL RADICALS. When two alkyl radicals meet, they may either combine or disproportionate. The latter reaction involves the transfer of a hydrogen atom from a radical to another to form equimolecular amounts of alkane and alkene, and might be classified as an ordinary metathetical reaction. Besides an activated complex for the disproportionation of ethyl radicals has been suggested[94,95] which resembles very much that of the attack of a methyl radical on ethane.

However, metathetical reactions are some 0 to 25 kcal/mole exothermic while disproportionations are much more. Thus the disproportionation of ethyl radicals is 58 kcal/mole exothermic. This large exothermicy makes the reactions occur with very small or zero activation energy. The A factor for the attack of a methyl radical on ethane is 10^{11} mole^{-1} cm^3 sec^{-1} while those for disproportionations are about 10^{13}. Due to those substancial differences, disproportionations are considered separatedly.

All quantitative studies on disproportionations involve the transfer of a hydrogen atom. Transfer of chlorine atom has been postulated[96], but autodisproportionation of perfluoro n-propyl radicals does not occur[97]. They will nevertheless cross-disproportionate with alkyl radicals to abstract a hydrogen atom[91].

The only absolute determination of the rate constant of a disproportionation reaction is that involving ethyl radicals[65]. The photolysis of diethyl mercury was used as radical source. With Shepp and Kutschke's value[67] for the combination reaction, the rate constant is given by

$$k_d = 10^{13.51} \exp(-800/RT) \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

In other cases an indirect aproach has to be used. Taking for instance

the disproportionation of isopropyl radicals

$$2\ iC_3H_7 \longrightarrow C_3H_6 + C_3H_8 \qquad d$$

they will also combine

$$2\ iC_3H_7 \longrightarrow C_6H_{14} \qquad c$$

it can be seen that

$$k_d = \frac{R_{C_3H_6}}{[iC_3H_7]^2} = \frac{R_{C_3H_8}}{[iC_3H_7]^2}$$

$$k_c = \frac{R_{C_6H_{14}}}{[iC_3H_7]^2}$$

hence

$$\frac{k_d}{k_c} = \frac{R_{C_3H_6}}{R_{C_6H_{14}}} = \frac{R_{C_3H_8}}{R_{C_6H_{14}}}$$

thus k_d/k_c ratios can be calculated if a suitable means of analysing the products is available. The situation becomes more complicated when a cross-disproportionation, that is to say that involving different radicals, is to be studied. The reaction is best followed by measuring the rate of formation of olefin and that of the dimer, as the alkane may be formed in other ways. This of course cannot be done when the source of radicals is the photosensitized hydrogenation of olefins where the reaction must be followed by measuring the rate of formation of alkane. Analysis of the products is best performed with the aid of gas chromatography.

Table 1. 2 gives a summary of results reported in the literature for disproportionations involving two like radicals. They all produce alkane and olefin. There is no reason however why the products should not be alkane and subs

tituted methylene. In fact such a disproportionation has been reported[98] involving acetonyl radicals.

$$2\ CH_3COCH_2 \longrightarrow CH_3COCH_3 + CH_3COCH$$

Disproportionation of unlike radicals can also be studied refering results to the rate of formation of their cross-combination product. The ratio of rate constants k_d/k_c is generally designated by Δ. When the notation $\Delta(Et, Pr^i)$ is used if refers to the reactions

$$C_2H_5 + iC_3H_7 \longrightarrow C_2H_6 + C_3H_6 \qquad d$$

$$C_2H_5 + iC_3H_7 \longrightarrow C_5H_{12} \qquad c$$

and

$$\Delta(Et, Pr^i) = \frac{k_d}{k_c} = \frac{R_{C_2H_6}}{R_{C_5H_{12}}} = \frac{R_{C_3H_6}}{R_{C_5H_{12}}}$$

Values of $\Delta(Alk', Alk'')$ are summarised in table 1. 3

It can be seing in tables 1. 2 and 1. 3 that there is a considerable disagreement between k_d/k_c ratios reported by different workers for the same reaction. This is not surprising considering the difficulties involved in the analysis of products and the mechanisms by which radicals are produced. It has been pointed out that sometimes radicals carry over an excess of energy from the process of their formation. It is not surprising that "hot" radicals would behave in a different way from those radicals produced in thermal equilibrium with their surroundings. In general, better agreement is found when the source of radicals is either aldehyde or ketone, and when the analysis has been carried out by means of gas chromatography.

Until recently, no temperature coefficient had been found for disproportionation to combination ratios $\Delta(Bu^n, Bu^n)$ has been reported to have an activation energy of 1.3 kcal/mole [39]. This rather surprising result does not seem to agree with posteriour publications [44]. The discussion of this and other aspects of disproportionations will be left until the discussion part of this thesis.

TABLE 1. 2 DISPROPORTIONATION OF LIKE RADICALS

Radical	SOURCE		T°C	k_d/k_c	Ref
ETHYL	diethyl ketone	P	25-300	0.14	99
			27-200	0.13	81
			100-250	0.12	75
			180-230	0.14	100
	azoethane	P	26-178	0.13	101
			27-118	0.12	102
	propionaldehyde	P	180	0.1	26
			50-315	0.15	40
	mercury diethyl	P	75-200	0.42	65
		T	350	0.13	103
	ethylene + H		20	0.15	104
			20	0.42	34
			20	0.1	105
			20	0.14	106
CH_3CD_2	, ' diethyl ketone-d_4	P	24-180	0.1	94
ETHYL-d_5	diethyl ketone-d_{10}	P	50-300	0.1	107
n-PROPYL	di-n-propyl ketone	P	30-108	0.3	108
			100-150	0.13	68
	n-butyraldehyde	P	25-190	0.16	37
	azo-n-propane	P	24-130	0.16	109
$CH_3CH_2CD_2$	2 pentanone 1,1,1,3,3-d_5	P	25-83	0.15	84
ISOPROPYL	mercury diisopropyl	T	230-440	1.0	5
	azoisopropane	P	20	0.5	110
			35-127	0.55	12
	propylene + H	+ H	290	0.7	111
			20	0.5	105
	diisopropyl ketone	P	25-150	0.63	21
	isobutyraldehyde	P	20-260	0.65	38
n-BUTYL	di-n-butyl mercury	P	140	1.5	112
	n-valeraldehyde	P	100	0.7	39
	methyl + n-butyl formate		70-195	0.94	44
ISOBUTYL	diisobutyl ketone	P	100	0.42	22
	isovaleraldehyde	P	26-124	0.17	30

TABLE 1. 2 DISPROPORTIONATION OF LIKE RADICALS (Continued)

Radical	SOURCE		T°C	k_d/k_c	Ref
sec-BUTYL	di sec-butyl mercury	T	490	0.7	114
	di sec-butyl ketone	P	100	2.27	22
	butene-2	+H	20	1.5	105
			20	0.95	113
	butene-2	+D	25	0.6	115
t-BUTYL	di-t-butyl ketone	P	100	4.59	22
			80	3.2	(b)
	isobutene	+H	20	2.2	105
	trimethyl acetaldehyde	P	27-230	4.38	28
n-PENTYL	n-pentane	-H	21	0.7	116
	methyl n-pentyl ketone	P	63-91	0.2	85
CYCLO PENTYL	cyclopentane	-H	30	0.2	33
METHYL CYCLOPENTYL	methyl-cyclopentane	-H	30	0.4	33
CYCLOHEXYL	cyclohexane	-H	30	0.5	33

P = Radicals produced by photolysis of radical source

T = Radicals produced by pyrolysis of radical source

-H = Radicals produced by photosensitized decomposition of alkane

+H = Radicals produced by photosensitized addition of H atoms to olefins.

TABLE 1.3 DISPROPORTIONATION OF UNLIKE RADICALS

Radicals	SOURCE		T°C	k_d/k_c	Ref
METHYL					
(Me, Et)	acetone-d_6 + diethyl ketone	P	27-200	0.08	81
	methyl ethyl ketone	P	25-240	0.04	79
	acetone + 2,2,4,4 diethyl ketone-d_4	P	90	0.06	80
(Me, Pr^n)	1,1,1,3,3 methyl n-propyl ketone-d_5	P	25-83	0.05	84
			35-300	0.32	82
(Me, Pr^i)	acetone + methyl isopropyl ketone	P	80-150	0.22	19
	methyl isopropyl ketone	P	100	0.17	125
(Me, Bu^n)	acetone + n-butyl formate	P	70-195	0.15	44
(Me, Bu^s)	butene-2	+H	25	0.30	113
			25	0.3	115
(Me, Bu^t)	di-t-butyl peroxide	P	20-60	0.85	13
	di-t-butyl peroxide + azomethane	P	25-79	0.88	117
	acetone + methyl t-butyl ketone	P	80-190	0.70	19
			80-190	0.81	118
(Me, $Pent^n$)	methyl n-pentyl ketone	P	63-91	0.1	85
(Me, CHO)	di-t-butyl peroxide + formaldehyde	T	123-147	0.25	119
(Me, CDO)	azomethane + formaldehyde-d_2	P	80-180	2.5	120
(Me, CH_3O)	methyl acetate	P	29	1.26 a	42
(Me, CD_3O)	methyl-d_3 acetate	P	30-90	1.4	77
(CD_3, CD_3O)	methyl-d_3 acetate	P	30-90	1.8	77
(Me, CH_3CO)	methyl-d_3 acetate	P	30	0.05	77
			29-217	0.06	42

a) this reference gives a value varying from 1.26 at 30°C to 2.6 at 142°C with E = 1.5 kcal $mole^{-1}$

TABLE 1.3 DISPROPORTIONATION OF UNLIKE RADICALS (Continued)

Radicals	SOURCE		T°C	k_d/k_c	Ref
(CD_3, CD_3CO)	1,1,1,3,3 methyl n-propyl ketone-d_5	P	25-83	0.01-0.055	84
(Me, Propoxyl)	diidopropyl peroxide	P		3.4	121
ETHYL					
(Et, Pr^i)	ethylene + propylene	+H	20	0.4	105
	diethyl ketone + isopropyl formate	P	34-150	0.43	45
(Et, Bu^t)	ethylene + butene-2	+H	20	0.6	105
	diethyl ketone + di-t-butyl ketone	P	80	0.5	(b)
(Et, Ethoxy)	ethyl propionate	P	29	1.3	122
ISOPROPYL					
(Pr^i, Et)	propylene + ethylene	+ H	20	0.6	105
	Unpublished results by Kerr and Trotman-Dickenson			0.2	
(Pr^i, Bu^s)	propylene + butene-2	+H	20	0.8	105
(Pr^i, Bu^t)	propylene + isobutene	+H	20	1.0	105
	diisopropyl ketone + di-t-butyl ketone	P	80	0.7	(b)
SEC-BUTYL					
(Bu^s, Pr^i)	propylene + butene-2	+H	20	0.8	105
(Bu^s, Bu^t)	propylene + isobutene	+H	20	0.5	105
t-BUTYL					
(Bu^t, Et)	isobutene + ethylene	+H	20	3.4	105
	diethyl ketone + di-t-butyl ketone	P	80	0.31	(b)

TABLE 1. 3 DISPROPORTIONATION OF UNLIKE RADICALS (Continued)

Radicals	SOURCE		T°C	k_d/k_c	Ref
(Bu^t, Pr^i)	isobutane + propylene	+H	20	2.4	105
	diisopropyl ketone + di-t-butyl ketone	P	80	0.67	(b)
(Bu^t, Bu^s)	isobutane + butene-2	+H	20	4.0	105
ETHOXYL					
(Eto, Et)	ethyl propionate	P	29	2.3	122
perfluoro-n-PROPYL					
(n-C_3F_7, Et)	di n-propyl ketone-F_{14} + ethane	P	100-180	0.4	91

P = Radicals produced by photolysis of radical source

T = Radicals produced by pyrolysis of radical source

+H = Radicals produced by photosensitized addition of H atoms to olefins.

1. 4 METATHETICAL REACTIONS OF ALKYL RADICALS. The type of reaction in which an alkyl radical R would react with a substrate molecule to give RH is undoubtedly the most widely studied type of alkyl radical reaction.

The only quantitative studies involve the transfer of a hydrogen atom, and most of the results presented refer to methyl radicals. Basically, the reaction scheme for the measurement of rate constants is as follows:

$$\text{Radical source} \longrightarrow R$$

$$2\,R \longrightarrow R_2 \qquad (1)$$

$$2\,R \longrightarrow RH + \text{olefin} \qquad (2)$$

$$R + XH \longrightarrow RH + X \qquad (3)$$

In practice it is never as simple as this; side reactions always complicate the system. RH is also produced by attack of the radical on the source, and sometimes in the primary photolytic act, as in the case of aldehydes. The olefin formed by reaction 2 may also be formed in the primary act, and by decomposition of the radical formed by hydrogen abstraction from the radical source. Each additional source of product introduces the need of a correction, and the errors in the calculation of results accumulate. The rate constant is finally obtained from the expresion

$$k_3/k_1^{\frac{1}{2}} = \frac{R_{RH}\ (\text{reaction 3})}{R^{\frac{1}{2}}R_2 \qquad [XH]}$$

The method applied to the study of methyl radical reactions has been extensively dealt with by Trotman-Dickenson [135,136]. Reactions of ethyl radicals are much more difficult to study. James and Steacie have described the method [100] for

radicals produced by photolysis of diethyl ketone, when the substrate is a molecule other than the radical source. Trotman-Dickenson [137] suggested another method involving partly deuterated diethyl ketone radical source. Since the rate of abstraction of secondary deuterium atoms in 2,2,4,4 tetradeutero diethyl ketone is so much faster than the rate of the primary hydrogen atoms, this partly deuterated ketone can be used instead of the fully deuterated compound, which is more difficult to obtain. In this case the product of the metathesis would be clearly distinguishable.

Considerations on metathetical reactions. The factors which determine the activation energies of transfer reactions are not well understood. Transition state theory does, however, satisfactorily predict the order of their A factors, which are 10^{11}-10^{12} mole^{-1} cm^{3} sec^{-1}. Differences between the rates at which two radicals attack a compound can be ascribed to a difference in the energies of activation, at least for methyl attack on alkanes. When ethyl radicals abstract hydrogen from alkenes [100] the differences are apparently due to changes in the A factors. There are however insufficient results to generalize this conclusion.

From results for methyl radicals produced in a variety of ways it can be said that radicals produced photolytically do not normally have an enhanced reactivity owing to an excess of energy carried over from the initial photolytic act.

The reactivities of the substrates RH closely follow the strengths of the R-H bonds. The rate constants always run methyl < primary < secondary < tertiary. A particularly full series of results showing this effect has been obtained with methyl radicals, as shown in table 1. 4. There is a less direct connection between the dissociation energy of the bond which is formed and the activity of the attacking radical.

The generalization that the activation energy of a transfer reaction is proportional to the strength of the bond to be broken was translated into quantitative terms by Polanyi who suggested that for a series of reactions, a relation should exist between the activation energy and the heat of one reaction. The relationship is

$$E = \alpha \Delta H + \text{constant}$$

where E is the activation energy and H the heat of the reaction. Resonance stabilization can be shown to be a major factor in determining activation energies of the reactions of many radicals. Polanyi's relationship might be expected to hold only if there is not such a resonance or if it is constant throughout the series. The reaction of methyl radicals with an alkane is a very symmetrical reaction as the bond broken is very much like the bond formed. α might be expected to be 0.5. It seems that the value is $\alpha \approx 0.35$ [162], although neither bond strengths nor activation energies are accurately known.

Trotman-Dickenson [138] proposed a relationship between the activation energies for the metathetical reaction of methyl radicals with alkanes and the strength of the relevant C-H bond. He obtained the straight line

$$E = 0.5 \Delta H + 12.5$$

but the C-H bond strengths were calculated by a questionable procedure [139]. Dainton, Ivin and Wilkinson [140] later extended this treatment but did not obtain a straight line relationship between the activation energies for a series of methyl radical abstractions and the heats of the reactions.

The transfer reactions of ethyl, propyl and butyl radicals are listed in

tables 1.5, 1.6 and 1.7. As already pointed out results are insufficient to support any generalizations. The variations of reactivity of n-heptane, 1-heptene and 1-heptyne is roughly as would have been expected on the basis of methyl radical results [136].

Differences between the reactivity of n and iso-propyl radicals seem smaller than might have been expected from values of $D(Pr^{n}-H)$ and $D(Pr^{i}-H)$.

The rates of attack of methyl, ethyl, n and isopropyl radicals on the corresponding azo-compounds have been found to be quite similar at about 100°C [109]. This striking result is not unique. The similarity in the reactivities of methyl, ethyl, n and isopropyl, and the butyl radicals in the H-atom abstraction from aldehydes has been recently noted by Birrell and Trotman-Dickenson [28]. The constancy of the rate constants must be connected with the exothermicity of the reactions.

TABLE 1. 4

The reactivities of Primary, Secondary and Tertiary Hydrogen atoms with Methyl Radicals in the gas phase.

Compound	Alkane	Alkene	Alkyne	Ether	Alcohol
Type of hydrogen					
Primary	0.3	5	7	1.5	2
Secondary	2.1	17	38	-	10
Tertiary	15.0	53	-	19.0	31

10^{-6} k / $mole^{-1}$ cm^3 sec^{-1} at 182°C per H atom

Summarized in ref. 46 from ref 136

TABLE 1. 5 METATHETICAL REACTIONS OF ETHYL RADICALS

Reactant	Radical Source		E	logA	$10^{-6}k$ 182°C	Ref
ETHYL						
deuterium	diethyl ketone	P	13.3	12.3	1	141
Hydrogen	diethyl ketone	P	(11.5)			141
	diethyl ketone-d_{10}	P	11.3	11.8	2	148
n-butane	diethyl ketone-d_{10}	P	10.4	11.3	0.4	107
isobutane	diethyl ketone-d_{10}	P	8.9	10.9	2	107
neopentane	diethyl ketone-d_{10}	P	12.6	11.6	5	107
n-hexane	diethyl ketone-d_{10}	P	10.1	11.4	3	148
cyclohexane	diethyl ketone-d_{10}	P	10.4	11.7	5	148
	diethyl ketone	P	8.2	11.8	72	100
n-heptane	diethyl ketone	P	10.6	12.0	8	100
heptene-1	diethyl ketone	P	8.3	11.5	32	100
heptyne-1	diethyl ketone	P	7.6	11.2	36	100
octene-1	diethyl ketone	P	8.3	11.5	32	100
trans-4-octene	diethyl ketone	P	8.7	11.8	42	100
propionaldehyde	propionaldehyde	P	5.9	11.1	182	40
propionaldehyde	propionaldehyde + di-t-butyl peroxide	T	7.6	11.8	141	142
methyl ethyl ketone	methyl ethyl ketone	P	8.0	11.3	28	79
diethyl ketone	diethyl ketone	P	7.8	11.4	45	75,99,100
	azoethane	P	7.6	11.3	44	143
$(CH_3CD_2)_2CO$	$(CH_3CD_2)_2CO$	P	8.7	11.9	51	94
$(CH_3CD_2)_2CO$	$(CH_3CD_2)_2CO$	P	11.7	11.7	4	94
diethyl ketone-d_{10}	diethyl ketone-d_{10}	P	9.0	11.3	10	107
	diethyl ketone-d_{10}	P	9.6	11.6	10	144
azoethane	azoethane	P	7.5	11.2	40	101
			8.0	11.6	20	102
diethyl mercury	diethyl mercury	P	6.2	10.6	42	65

TABLE 1. 5 METATHETICAL REACTIONS OF ETHYL RADICALS (Continued)

Reactant	Radical Source		E	logA	$10^{-6}k$ 182°C	Ref
C_2F_5						
Hydrogen	$(C_2F_5)_2CO$	P	11.9	12.7	10	87
methane	$(C_2F_5)_2CO$	P	10.6	11.6	3	87

Results are based on $k_c = 10^{14.0}$ mole^{-1} cm^3 sec^{-1} for ethyl radical combination.

The atoms underlined are those attacked in the metathesis.

T = radicals produced by thermal decomposition.

P = radicals produced by photolysis.

TABLE 1. 6 METATHETICAL REACTIONS OF PROPYL RADICALS

Reactant	Radical Source		E	logA	$10^{-6}k$ 182°C	Ref
ISOPROPYL						
Hydrogen	propylene	↓H	12.5			111
iso $C_3H_7.C\underline{H}O$	isobutyraldehyde	P	6.3	11.3	186	38
iso $C_3\underline{H}_7.CHO$	isobutyraldehyde	P	9.5	11.2	4	38
azo-isopropane	azo-isopropane	P	6.5	10.4	19	110
			6.1	10.5	34	12
$(CH_3)_2C\underline{D}_2\ 2CO$	$(CH_3)_2CD\ 2CO$	P	9.3	11.1	4	21
$(C\underline{H}_3)_2CD_2\ 2CO$			11.7	11.8	5	21
n-PROPYL						
n $C_3H_7C\underline{H}O$	n-butyraldehyde	P	6.7	11.3	120	37
n $C_3\underline{H}_7CHO$	n-butyraldehyde	P	10.8	11.3	1	37
di-n-propyl ketone	di-n-propyl ketone	P	6.5	10.7	38	20
azo-propane	azo-n-propane	P	7.9	11.6	61	109
n-C_3F_7						
Hydrogen	$(C_3F_7)_2CO$	P	12.3	12.6	5	145
Deuterium	$(C_3F_7)_2CO$	P	13.8	12.8	2	145
Methane	$(C_3F_7)_2CO$	P	9.5	11.0	3	91
ethane	$(C_3F_7)_2CO$	P	9.2	12.2	60	91
Cyclohexene	$(C_3F_7)_2CO$	P	5.2	11.1	400	147

Results based on $k_c = 10^{14.0}$ $mole^{-1}$ cm^3 sec^{-1} for propyl radical combination

The atoms underlined are those attacked in the metathesis.

↓H = radicals produced by mercury photosensitized addition of hydrogen atoms to olefins.

P = radicals produced by photolysis.

TABLE 1. 7 METATHETICAL REACTIONS OF BUTYL RADICALS

Reactant	Radical Source		E	log A	$10^{-6}k$ 182°C	Ref
n-BUTYL						
n-valeraldehyde	n-valeraldehyde	P	5.4	10.9	200	39
sec-BUTYL						
1-methyl butyraldehyde	1-methyl butyraldehyde	P	4.9	10.7	219	36
i-BUTYL						
di-iso-butyl ketone	di-iso-butyl ketone	P	7.6	11.4	55	22
$i\text{-}C_4H_9\cdot\underline{C}HO$	isovaleraldehyde	P	6.5	11.7	400	30
$i\text{-}C_4\underline{H}_9\cdot CHO$	isovaleraldehyde	P	12.6	12.7	4	30
t-BUTYL						
$t\text{-}C_4H_9\cdot\underline{C}HO$	pivalaldehyde	P	4.3	10.5	250	28
$t\text{-}C_4H_9\cdot CHO$	pivalaldehyde	P	10.0	11.9	12	28

Results are based on $k_c = 10^{14.0}$ $mole^{-1}$ cm^3 sec^{-1} for butyl radical combination

The atoms underlined are those attacked in the metathesis.

P = radicals produced by photolysis.

1. 5 ADDITION REACTIONS OF ALKYL RADICALS TO MULTIPLE BONDS. The difficulties normally found in the determination of rate constants for radical reactions are greatly increased in additions and in decompositions of radicals, reactions in which not only the reactants but also the products are radicals. Consideration of the diversity of reactions that such radicals may undergo makes it clear that the determination of their rate of formation is complex. It is not surprising then that our present knowledge of addition of alkyl radicals to unsaturated compounds is comparatively small in view of the interest and importance of polymerization reactions.

The reactions can be followed by investigating the fate of all radicals released into the system. By comparison of results in the presence and absence of unsaturated the rate of formation of the addition product can be deduced. Another way consists on measuring the olefin consumed during the reaction. The errors involved in both these calculations are large. A third approach to the problem involves the determination of the rates of formation of the products by direct analysis which is a much more satisfactory method.

The material balance method has been used by Steacie et al. [124,149] to investigate some addition reactions of methyl and ethyl radicals using the corresponding dialkyl ketones as photolytic sources of radicals. The simple reaction mechanism for dialkyl ketone photolysis is

$$C_2H_5COC_2H_5 + h\nu \longrightarrow 2\,C_2H_5 + CO$$
$$2\,C_2H_5 \longrightarrow C_4H_{10}$$
$$2\,C_2H_5 \longrightarrow C_2H_4 + C_2H_6$$
$$C_2H_5 + C_2H_5COC_2H_5 \longrightarrow C_2H_6 + C_2H_5COC_2H_4$$
$$C_2H_5 + C_2H_5COC_2H_4 \longrightarrow C_4H_9COC_2H_5$$

It was found experimentally that

$$\frac{R_{C_2H_6} + R_{C_4H_{10}}}{R_{CO}} = 0.997 \pm 0.03$$

In the presence of an olefin ethyl radicals add across the double bond to form a larger alkyl radical which will in its turn react with other ethyl radicals or will form stable products in some other way. In either case two ethyl radicals are consumed for each molecule of olefin which reacts, and neither of them will produce ethane nor butane.

The material balance then becomes

$$(R'_{C_2H_6} + R'_{C_4H_8} + R'_A)/R_{CO} = 1$$

where R'_A is the rate of formation of the addition product and R'_X indicates the presence of unsaturate in the system. Under these conditions the rate constant is calculated from the equation below.

$$\frac{k_{add}}{k^{\frac{1}{2}}_{comb}} = \frac{R_{CO} - (R_{C_4H_{10}} + R_{C_2H_6})}{[olefin]\ R^{\frac{1}{2}}_{C_4H_{10}}}$$

If ethane or ethylene is formed by cross disproportionation of ethyl with the radical product of the addition reaction then that equation will give artificially small values of addition rates. Experimental evidence seems to indicate that such reaction may be neglected [149].

The method cannot be so readily applied to the photolysis of acetone because

the stability of the acetyl radical restricts the temperature range. Mandelcorn and Steacie [124] applied the method to the photolysis of acetone in the presence and absence of unsaturate, but they also measured the consumption of olefin whicl is supposed to react with methyl radicals only but which might polymerize or react with acetonyl radicals. With this they placed an upper limit on the rate of addition. The agreement between the values obtained in either way for addition of methyl radicals to ethylene, propylene, butadiene and acetylene was reasonably good.

More recently Brinton [83] has calculated the rate of addition of methyl radicals to ethylene in a system in which di-t-butyl peroxide was the thermal source of radicals. Analysis of the products was made by low temperature distillation and mass spectrometry. Brinton hoped that by keeping the concentration of ethylene low it would be possible to limit the polymerization of ethylene to the initial addition of methyl. n-Hexane was however found at all ethylene concentrations. It can only be explained by propyl addition to ethylene followed by combination of n-pentyl with methyl radical and by combination of two propyl radicals. By calculating the extent of these hexane forming reactions, Brinton derived a rate constant for methyl addition to ethylene.

The value of the rate constant at 142°C derived from the work of Mandelcorn and Steacie is the same as that obtained by Brinton, although the Arrhenius parameters suggested by Brinton are to be prefered since his method was more direct.

Another method which has been widely applied to the investigation of rates of addition of radicals to unsaturates is based on the high reactivity of the hydrogen atom of an aldehydic group. With this method, additions of larger alkyl

radicals to ethylene and acetylene have been studied by Trotman-Dickenson et al. [48]. A description of the method can be found in chapter III of this thesis. In the case of acetylene no further addition of the alkenyl radical was observed in appreciable amounts. The addition of radicals to ethylene produces a radical which reacts with the olefin to form about 10% of a higher alkyl radical. Correction for this further addition as well as for dimerization, combination with other radicals and disproportionation was made in the calculation of rates of addition.

The most notable feature of the addition reactions is the constancy of the rate constants despite considerable variations in the nature of the bond attacked and in the structure of the radical and of the unsaturate. It is likely that some of the variations in A and E in table 1.8 are due to experimental errors.

Despite this regularity the results of attack of ethyl radicals on olefins show significant variations similar to those found in other addition series[46]. 1,2,disubstituted ethylene is less reactive than the monosubstituted; substitution in 1,1 positions generally increases the reactivity; the effect is greatly acentuated in tri and tetrasubstituted compounds. In general, trans disubstituted ethylenes are more reactive than the corresponding cis compounds.

Addition of radicals in the liquid phase. The results of addition of alkyl radicals to olefins in solution are much more extensive. Most of these have been obtained by Szwarc and his collaborators by a variant of the material balance method. They pyrolyzed acetyl peroxide in iso-octane solution. For each molecule of peroxide two molecules of carbon dioxide are formed. Ethane is pro

duced by "cage" recombination of two methyl radicals. Methane is formed by abstraction of hydrogen from the solvent:

$$CH_3 + C_8H_{18} \longrightarrow CH_4 + C_8H_{17} \qquad (a)$$

In the presence of an unsaturate, reaction (b) takes place reducing the yield of methane

$$CH_3 + U \longrightarrow CH_3U \qquad (b)$$

It can be shown that

$$k_b/k_a = \frac{(R_{CH_4}/R_{CO_2})_X - (R_{CH_4}/R_{CO_2})_Y}{(R_{CH_4}/R_{CO_2})_Y} \cdot \frac{C_8H_{18}}{U}$$

where the subscripts X and Y denote the absence and presence respectively of unsaturate.

Similar ratios k'_b/k'_a can be derived from gas phase results for k (abstraction from the parent aldehyde)/k (addition to ethylene).

The use of this relation presupposes that all aldehydic hydrogen atoms are equivalent. The constancy of the rate constants for methyl attack shows that the structure of the alkyl group has little effect on the reactivity of the aldehydic hydrogen [150]. Hence we get the following table where U is benzene:

Radical	Me	Et	Pr^n	Pr^i	Bu^n	Bu^t
k'_b/k'_a (142°C)	0.45	0.33	0.50	0.63	0.16	0.34 (a)
k_b/k_a (65°C)	0.29	2.9	2.0	6.0 (35°C)	-	-

(after Kerr and Trotman-Dickenson, ref[48]. (a), calculated by writer from ref [28]).

The marked differences in the two sets of results cannot be attributed to the change from gas to liquid phase. The variations in solution are most probably due to the different rates of hydrogen abstraction from iso-octane by the alkyl radicals.

TABLE 1. 8 ADDITION REACTIONS OF ALKYL RADICALS TO MULTIPLE BONDS

a) Addition to olefins

Radical	Reactant	Radical Source		E	logA	$10^{-6}K$ (142°C)	Ref
METHYL							
	ethylene	acetone	P	7.0	11.2	33	124
		DTBP	T	8.7	12.1	33	83
	propylene	acetone	P	6.0	10.8	44	124
	butadiene	acetone	P	2.5	9.7	240	124
ETHYL							
	ethylene	ethylene	+H	5.5	10.0	13	151
		azoethane	P	5.5	10.3	31	152
		propionaldehyde	P	8.6	12.1	38	40
	hexene-1	diethyl ketone	P	6.8	10.9	21	149
	heptene-1	diethyl ketone	P	7.0	11.1	26	149
	2,3,3 trimethyl butene-1	diethyl ketone	P	5.6	10.2	18	149
	octene-1	diethyl ketone	P	6.7	10.9	23	149
	2,4,4,trimethyl pentene-1	diethyl ketone	P	5.7	10.6	40	149
	styrene	diethyl ketone	P	4.0			153
	vinyl acetate	diethyl ketone	P	6.8			153
n-PROPYL							
	ethylene	n-butyraldehyde	P	6.5	10.9	30	37
s-PROPYL							
	ethylene	isobutyraldehyde	P	6.9	11.4	59	38
n-BUTYL							
	ethylene	n-valeraldehyde	P	7.3	11.1	18	39
t-BUTYL							
	ethylene	pivalaldehyde	P	7.1	11.2	25	28

TABLE 1. 8 ADDITION REACTIONS OF ALKYL RADICALS TO MULTIPLE BONDS (Continued)

b) Addition to acetylenes

Radical	Reactant	Radical Source		E	logA	$10^{-6}K$ (142°C)	Ref
METHYL							
	acetylene	acetone	P	5.5	11.0	124	124
		acetaldehyde	P	7.8	11.4	20	(a)
ETHYL							
	acetylene	propionaldehyde	P	7.2	11.1	20	(a)
	heptyne-1	diethyl ketone	P	8.8	11.9	20	149
iso-PROPYL							
	acetylene	isobutyraldehyde	P	6.9	11.2	37	(a)
t-BUTYL							
	acetylene	pivalaldehyde	P	5.4	10.7	71	(a)

Results are based on $K_c = 10^{13.34}$ mole^{-1} cm^3 sec^{-1} for methyl radicals combination.

All other results based on $K_c = 10^{14.0}$ for radical combination.

E in Kcal. mole^{-1}

A in mole^{-1} cm^3 sec^{-1}

DTBP = di-t-butyl peroxide

P = radicals produced by photolysis

T = radicals produced by pyrolysis

1. 5 DECOMPOSITION OF ALKYL RADICALS. When the temperature of the system is increased sufficiently the radicals present will start to decompose yielding a hydrogen atom, a methyl or an ethyl radical, together with an olefin. Propyl radicals would be formed in the decomposition of pentyl but so far no such reaction involving radicals larger than butyl have been studied.

Decompositions to radicals have activation energies of the order of 20-35 kcal/mole and those which yield hydrogen atoms of about 40-45 kcal/mole. The different values are connected with the different strengths of the C-C and C-H bonds.

The difficulties involved in the study of this type of reactions have already been pointed out. Complicating side reactions become so important at the high temperatures at which decompositions take place (above 200°C for thermally equilibrated radicals) that it is not surprising that until recently all information about decompositions came from Bywater and Steacie's publications on the mercury photosensitized decomposition of paraffins [31]. They produced radicals from ethane, propane, n-butane and isobutane at temperatures from 30 to 500°C.

At room temperature excited mercury atoms react with alkane molecules:

$$Hg + RH \longrightarrow Hg + R + H \qquad (1)$$

The hydrogen atoms produced may either combine in a three-body collision (2) or form a hydrogen molecules by abstraction of a hydrogen atom (3)

$$H + H + M \longrightarrow H_2 + M \qquad (2)$$

$$H + RH \longrightarrow H_2 + R \qquad (3)$$

The alkyl radicals will combine or disproportionate

$$\left.\begin{aligned} 2R &\longrightarrow R_2 \\ &\longrightarrow RH + r \end{aligned}\right\} \quad (4)$$

where r is an olefin. As the temperature increases reaction (3) becomes more important and the quantum yield for the formation of hydrogen approaches unity. The conversion of the alkane must be kept low since the quenching cross-sections of alkenes and hydrogen are relatively high.

At high temperatures decomposition starts:

$$\left.\begin{aligned} R &\longrightarrow H + r \\ &\longrightarrow R' + r' \end{aligned}\right\} \quad (5)$$

Reaction of R' or H with the alkane will regenerate the radical R.

According to the above scheme the number of radicals removed by combination and disproportionation (reaction 4) is equal to twice the number of hydrogen molecules formed at low temperature where decomposition does not take place. Thus

$$[R] = (R_{H_2}/k_4)^{\frac{1}{2}}$$

As the only chain ending reactions at all temperatures are those involving two radicals, the number of radicals reacting by (4) can be calculated at high temperatures by extrapolation of the rate of formation of non-chain hydrogen, i.e. that produced at low temperatures.

The rate of decomposition by reactions 5 is equal to RH , the rate of formation of hydrogen in excess of that produced at low temperatures and estimated by extrapolation, or to $R_{R'H}$ which can be directly measured. Hence

$$k_5/k_4^{\frac{1}{2}} = R_{R'H}/R_{H_2}^{\frac{1}{2}} \quad \text{or} \quad R_{H_2}/R_{H_2}^{\frac{1}{2}}$$

This method of measuring k_5 has several disadvantages: there is always uncertainly about which radical is formed and thus whose decomposition is being measured. Besides the reaction volume is never known; if the concentration of mercury atoms is that corresponding to the saturated vapour pressure at room temperature, 95% of the light will be absorbed in the first 3 cm of cell. The reaction volume has to be assumed to extend 2.5 cm from the window through which the light enters [154].

The other general method of studying decompositions is the photolysis of aldehydes, first used by Gruver and Calvert [36] and later extended by Trotman-Dickenson and his collaborators. The method is direct because both of the products of decomposition are directly measured. The concentration of radicals is often estimated from the rate of formation of RH by attack of the radical R on the aldehyde because the rate of formation of the dimer is usually too small at the high temperatures used. Small corrections have generally to be applied to account for the H_2, R'H, r and r' formed in the initial photolytic acts. Calvert and Sleepy [41] by photolysing selectively azomethane in the presence of n-butyraldehyde have overcome those difficulties.

The photolysis of the corresponding dialkyl ketones has yielded information on the decompositions of n-propyl and s-propyl radicals. The methods of obtaining the results are analogous to that used with aldehyde photolysis.

Information on the n-propyl radical has also been obtained by Durham, Martin and Sutton [155]. Propyl bromide was reacted with sodium in a flow system and on emerging from a tube at known temperature the radical reactions were quenched

by injection of radiactive iodine into the gas stream. The products were analysed by radio-chemical techniques for propyl iodide and methyl iodide and the portion of radicals decomposing in a given time at a known temperature was obtained. Hence an activation energy was found.

Quite recently Kerr and Calvert [109] photolysed azo-n-propane and from the results they deduced an activation energy and A factor for the decomposition of n-propyl to methyl and ethylene.

Results for the different radicals and moles of decomposition are summarized in table 1. 9. It can be observed that values obtained by mercury photosensitized decomposition usually lie between those for the two isomeric radicals that could have been formed. Both radicals are therefore most certainly present in roughly equal amounts in the system and the results are not very useful for the purpose of establishing the effect of structure on rate of reaction.

Activation energies and A factors for decomposition reactions can be calculated from a knowledge of the corresponding addition to olefins and with the aid of thermodynamic data.

The A factor of a reaction such as (6) is related to that of

$$C_3H_7 \longrightarrow CH_3 + C_2H_4 \qquad (6)$$

the back reaction (-6) by the expression

$$\Delta S_6 = R\ln (A_6/A_{-6})$$

Calculation of entropies of radicals by standard methods give values of A_6 of about 10^{13} sec^{-1}, the normal value for unimolecular reactions according

to the Slater theory.

The activation energies and heat of reaction are connected by the equation

$$\Delta H_6 = E_6 - E_{-6}$$

Besides

$$\Delta H_6 = \Delta H_f^\circ(CH_3) + \Delta H_f^\circ(C_2H_4) - \Delta H_f^\circ(C_3H_7)$$

Heats of formation of radicals can be deduced from a knowledge of the C-H bond strengths whose rupture in a paraffin would produce the radical. Table 1.9 shows the close relationship which exists between H and E except in those reactions which involve a rearrangement of the radical or activated complex. It has been seen in the previous section that E_{-6} can be approximately taken as 7 kcal.mole^{-1}. Experimental evidence seems to indicate that additions of H and CH_3 occur with activation energies which do not differ by more than one or two kcal.mole^{-1}. In consequence it seems clear that most activation energies have been underestimated. In those radicals which require a rearrangement of hydrogen atoms some sort of temperature coefficient should be associated with the process. Consequently the experimental activation energies of those reactions are also probably too low. The rearrangement may occur before or during decomposition. In the former case it should be possible to detect the other products of the rearranged radicals, although they might decompose before deactivation by collision occurs.

If rearrangement is a simultaneous process with decomposition then addition of radicals to olefins which is supposed to occur via the same type of activated complex would be expected to yield rearranged products. Brinton [83] did not

find isobutane in decisive amounts when methyl radicals at high concentration react with ethylene. We have repeated the experiments at still higher radical concentrations and arrived at the same conclusion. Perhaps the experiments should be repeated at lower pressures and higher temperatures. Isomerization of the radical formed when isopropyl or t-butyl radicals add to acetylene has been found to occur with a definite temperature coefficient. Isomerization of radicals larger than butyl has also been reported (see chapter V of this thesis)

The rate constants for decomposition to hydrogen show marked regularities except for ethyl where it largely depends on the rate of transfer of energy to a small molecule. The same regularity is observed in the decomposition to methyl. Decomposition of isopropyl and t-butyl, which require rearrangement are slow, while that of n-butyl to propene is much faster, probably due to a different mechanism. Isopropyl and t-butyl can only decompose after a three-centre transfer of a hydrogen atom between adjacent carbons. n-Butyl can rearrange by a four-centre process, similar to that involved in the disproportionation of ethyl radicals, which involves much less strain.

Decomposition reactions of radicals are interesting because they might provide useful information on the validity of the theories of unimolecular reactions. The dependance of the rate of decomposition on total pressure is well known. On the other hand some A factors reported seem in good agreement with the Slater theory which in its approximate form restricts the limiting rate of unimolecular decompositions to the highest frecuency of normal vibration within the molecule [156]. "High" A factors found by some workers seem to be accounted for by the model based on the theories of Hinshelwood, Kassel, Rice, Ramsperger and Marcus [157] which allow free energy exchange between the different energy modes.

TABLE 1. 9 DECOMPOSITION OF ALKYL RADICALS

Radical	H	E	logA	$10^{-2}K$ at 400 °	Ref
Loss of hydrogen atom					
ETHYL	39	40	14.0	16	31
		31	11.2	13	40
n-PROPYL	37	38	14.6	200	31
		35	13.6	159	37
i-PROPYL	41	37	13.8	63	38
		38	14.6	200	31
		35	13.1	50	21
n-BUTYL	36	high			31
s-BUTYL	40	high			31
i-BUTYL	35	31	13.0	8.4	30
t-BUTYL	42	44	16.3	0.6	28

TABLE 1. 9 DECOMPOSITION OF ALKYL RADICALS (Continued)

Radical	H	E	logA	$10^{-2}k_o$ at 400 ^{o}	Ref
Loss of Methyl Radical					
n-PROPYL	25	20	9.2	5	31
		19	-	-	20,155
		25	11.7	32	37
		35	15.8	316	41
		35	15.4	100	109
i-PROPYL	29	20	9.2	5	31
		30	10.6	0.1	38
		33	12.0	0.25	21
n-BUTYL	22	23	11.2	55	31
		27	12.1	20	39
s-BUTYL	26	23	11.2	55	31
		24	11.7	76	36
		31	15.7	4000	158
i-BUTYL	25	26	12.8	213	30
		19	8.7	5	31
t-BUTYL	32	46	16.0	0.1	28
		19	8.7	5	31
Loss of Ethyl Radicals					
n-BUTYL	23	23	11.2	55	31
		22	11.2	120	39

H and E in kcal.mole^{-1}

A and k in sec^{-1}

CHAPTER II

GENERAL EXPERIMENTAL

2.1. KINETIC APPARATUS. The apparatus as shown in fig. 2.1 was a high vacuum static system. A two stage mercury diffusion pump backed by a "Hy-vac" rotary oil pump pumped the apparatus down to pressures about 10^{-5}mm Hg, as measured in a gas burette used as a McLeod gauge. Pyrex glass was used throughout the apparatus. The cylindrical quartz reaction vessel (R. V.) with two parallel flat windows was housed in a coaxial furnace, electrically heated. Its volume was 164 c.c. The heating wire of the furnace was divided into three sections in series so that it could be heated either along the length of the furnace or only at both ends, should the central part become too hot. Altering the voltage by means of a variac, the temperature of the reaction vessel could be changed. One end of the furnace contained a quartz window. The temperature in the furnace was measured by means of a thermocouple constructed from commercial T_1/T_2 wires. The hot junction was placed inside a glass tube above the reaction vessel and could be moved along the length of the furnace. The cold junction was maintained at about 20°C inside a thermos flask containing water. The potential differences were measured on a Tinsley D.C. Potentiometer with a Doran Galvanometer. Temperatures were calculated using the calibration tables supplied by the manufacturers of the thermocouple wires.

The lamp used for the photolysis was a 125W 230V OSRAM Mercury lamp type MB/U whose glass bulb had been removed. It was allowed to warm up for twenty minutes before each run was started. In most of the runs the

light was unfiltered and was focussed with a quartz lens of 10 cm focal length. It entirely filled the reaction vessel. A sheet of pyrex glass 1 mm thick was placed between the lamp and the lens in some cases. An aluminium foil reflector increased the intensity of the light.

Two gas sample storage bulbs (G.S.B.) and liquid sample reservoir (L.S.R.) were connected to the reaction vessel. The pressure of the reactants could be measured either with a differential manometer butyl phthalate/mercury magnifying type for pressures up to 70 mm Hg or else with an ordinary mercury manometer for higher pressures. Standard calibration of the differential manometer showed a sensitivity of 7.57 cm per cm of mercury.

All tubing connecting different parts of the reaction system was kept at about 100°C by means of an electrically heated wire, except in runs in which acetaldehyde or propionaldehyde were photolysed.

2.2. ANALYTICAL SYSTEM. The reaction vessel was connected with an analytical system which consisted of a train of four traps. The last trap could be used with liquid oxygen boiling at reduced temperature. Between the first and second trap, a two-stage mercury diffusion pump was situated. Gases passing through the traps could be led either to the vacuum line or to a gas burette through a non-return mercury float valve by means of a Töepler pump. The volumes of the different parts of the gas burette according with the diagram were as follows:

A	=	0.276	cm^3
A + B	=	0.512	cm^3
A + B + C	=	4.225	cm^3

A + B + C + D	= 20.95	cm^3
E	100.	cm^3
G	250.	cm^3

The gas burette was used as a McLeod gauge to check the vacuum before each run was started.

Gases frozen down in the traps were passed through aldehyde and acetylene absorbents and then trapped into a tapped container. The condensable products of the runs were analysed by gas chromatography. The aldehyde absorbent was prepared from 25–50 mesh firebrick on which 25% by weight of a paste of sodium bisulphite in ethylene glycol was suspended. The acetylene absorbent was prepared in the same way by suspending 25% by weight of a saturated solution of silver nitrate in ethylene glycol on 20–30 mesh firebrick.

A low vacuum line was connected to points marked LV in the diagram.

2.3 GAS CHROMATOGRAPHY APPARATUS. Figure 2.2 shows a diagram of the apparatus. The carrier gas, hydrogen from a commercial cylinder, was split passing on the one hand to a mercury bubbler which controlled the pressure, and on the other hand through a flow regulator, a series of buffering vessels constructed from small tubes joined up with very fine capillary tubing which served to iron put all irregularities from the flow, and a tube containing Linde molecular sieves to remove humidity. The dry gas was passed through the reference cell of the thermal conductivity gauge into the inyection system, which consisted in a W tube which could either be by passed while being connected to the vacuum line or inserted in the flow of carrier gas. Then the gas was passed through the column, the second cell and again through buffering vessels to increase the stability of the base line in the recorder. A flow meter was placed at the end. The

flow rate was kept at 30 $\pm$ .3 ml/min.

The thermal conductivity cell consisted of a solid brass block through which two identical channels were drilled. Stretched along similar parts of each channel were tungsten filaments of about 10 ohms resistance. The electrical circuit for the conductivity cell is shown in fig. 2.3. The voltage for the Wheatstone bridge circuit was supplied by two two-volt batteries and was maintained at 3.90 v by means of a two ohm variable resistance in series. The filaments of the conductivity gauge formed two arms of the bridge, and the other two arms consisted of approximately 100 ohms resistances. The 10.000 ohms rheostat across one of these 100 ohms resistances was used to adjust the balance of the bridge. The off-balance current set up when a gas mixed with the hydrogen passed through the analysing cell was fed into a 1 mV Sunvic potentiometric recorder via a voltage divider, by which a change in sensitivity of approximately five could be effected.

The conductivity cell was placed inside a 600 ml beaker which was then filled up with firebrick powder. This beaker was wound with heating tape which enabled the catharometer to be heated up to about 200°C and was placed inside a 1 l. beaker, containing firebrick powder. The whole thing was then introduced inside a can with ordinary cotton wool and glass wool covered the can, thus ensuring a constant temperature in the conductivity cell which was heated with the two hot tungsten filaments exclusively.

2.4 CHROMATOGRAPHIC CALIBRATIONS. Before any quantitative determination could be done, a series of calibrations were necessary for each compound. The procedure consisted of introducing measured volumes of sample into the inyec-

tion system of the apparatus. A small gas burette attached to the apparatus was used. The sample was then analysed and the area of the peak was measured with a planimeter. In the case of ethane, which produced a very sharp peak in the chromatograms the height was plotted against the amount of sample. A straight line was obtained for each compound. When a change of column was necessary, or the same column was heated at a different rate during the chromatogram, no change in the calibration curve was observed even when a change in the retention time of the particular compound accompanied the change of column.

The gases used for calibrations were as follows:

Ethylene, propylene, propane, isobutane, isobutene and n-butane from commercial cylinders, were shown to be pure by gas chromatography. They were degassed and then distilled under vacuum rejecting head and tail franctions.

Ethane from a commercial cylinder contained 5% of ethylene. It was supposed that the total amount was proportional to the sum of the heights of the peaks obtained in the chromatograms. The error thus introduced was negligible.

Propylene and isobutene were also prepared by dehydrating the corresponding alcohol with phosphorous pentoxide. The gas was passed through a trap at -70°C and then condensed at liquid oxygen temperature. The samples thus obtained were shown to be pure by gas chromatography.

Isopentene, 2,3 dimethyl butane, 4, methyl pentane and 2,2,4, trimethyl pentane were commercial samples shown to be pure by gas chromatography.

Isopentane was a commercial sample containing 10% of another pentane; both

peaks were measured for calibration purposes (See notes 1 and 2).

Notes.-

1) It was found that in some cases, saturated hydrocarbons have the same sensitivity as the corresponding unsaturated ones i.e. isopentane and 3,methyl butene-1 etc. It is here assumed that this is true for all other cases except for propane and propylene and ethane and ethylene.

2) It was also found that isomeric hydrocarbons have the same sensitivity, within experimental error (2%) i.e. n-butane and isobutane etc.

2.5 PROCEDURE FOR A RUN. Before any run was started, the apparatus was pumped down to a pressure of 10^{-4} mm Hg with the absorbent containers open to the main vacuum line, and then to 10^{-5} mm Hg or less, for the rest of the apparatus.

The reactants which were kept at liquid oxygen temperature (liquid nitrogen for trimethylacetaldehyde and the ketones) were warmed up. The reactant with the highest boiling point was allowed into the reaction vessel, and the pressure noted. If a second reactant had to be used it was then introduced and the pressure reading again taken. When an inert gas was necessary, N_2 was introduced and the pressure again measured. The run was started by removing a shutter placed between the lens and the window of the furnace. At the same time a stop-watch was started, and the temperature taken. When the run was only of a few minutes, a single temperature reading was taken, but for longer ones, it was noted several times during the experiment and a mean value was calculated and taken as the temperature of the run. An increase of one to two degrees was observed during the run, depending on the temperature. When the reaction had reached the desired stage, the run was finished by switching off the lamp.

Simultaneously, the time reading was taken.

Collection and analysis of products.-

a) Photolysis of aldehyde/acetylene mixtures. The products from the reaction passed to the analytical system where all traps were kept at liquid oxygen temperature. Liquid nitrogen was used after run 96, at the begining of the photolysis of trimethylacetaldehyde. The non-condensable gases passed straight through to the vacuum line. In the case of acetaldehyde/acetylene mixtures, liquid oxygen boiling under reduced pressure was placed round the last trap and non-condensable gases were drawn through with the Töepler pump. When all the non-condensable gases had been pumped down, the first trap was warmed up and the products distilled into the second one, while still pumping down. This was succesively done until all products were condensed in the last trap. The accomplishment of the collection was checked by means of a McLeod gauge. They were passed through acetylene and aldehyde absorbents and then analysed by gas chromatography.

b) Photolysis of ketones. Products and reactants were condensed at liquid nitrogen temperature in all traps, while non-condensable gases passed through to the main vacuum line. When ethylene was one of the products which had to be measured, liquid oxygen boiling at reduced pressure was placed round the last two traps. Once the non-condensable gases had been removed, the products were allowed to distil from the first to the second trap, and then to the third. Collection of products was checked by means of a McLeod gauge placed before the third trap. Now by warming up traps number three and four, excess of ketones and products of the reaction were condensed into the tapped container and subsequently into the inyection system for gas chromatographic analysis.

2.6 SPECIMEN RUN.

(Photolysis of isobutyraldehyde/acetylene mixture)

Furnace temperature	386.5	^{o}K
Room temperature	293.0	^{o}K
Isobutyraldehyde pressure	18.44	mm Hg
Acetylene pressure	25.68	mm Hg
[Acetylene] =	1.342×10^{-6}	mole cm^{-3}
length of run	600	seconds

Analysis by Gas Chromatography

Product	peak area in square inches	μ Moles of product	Rate of formation 10^{12} mole cm^{-3} sec^{-1}
isopentene	0.305	0.69	7.011
n-pentene	0.085	0.2	2.032
hexane	0.61	0.91	9.247

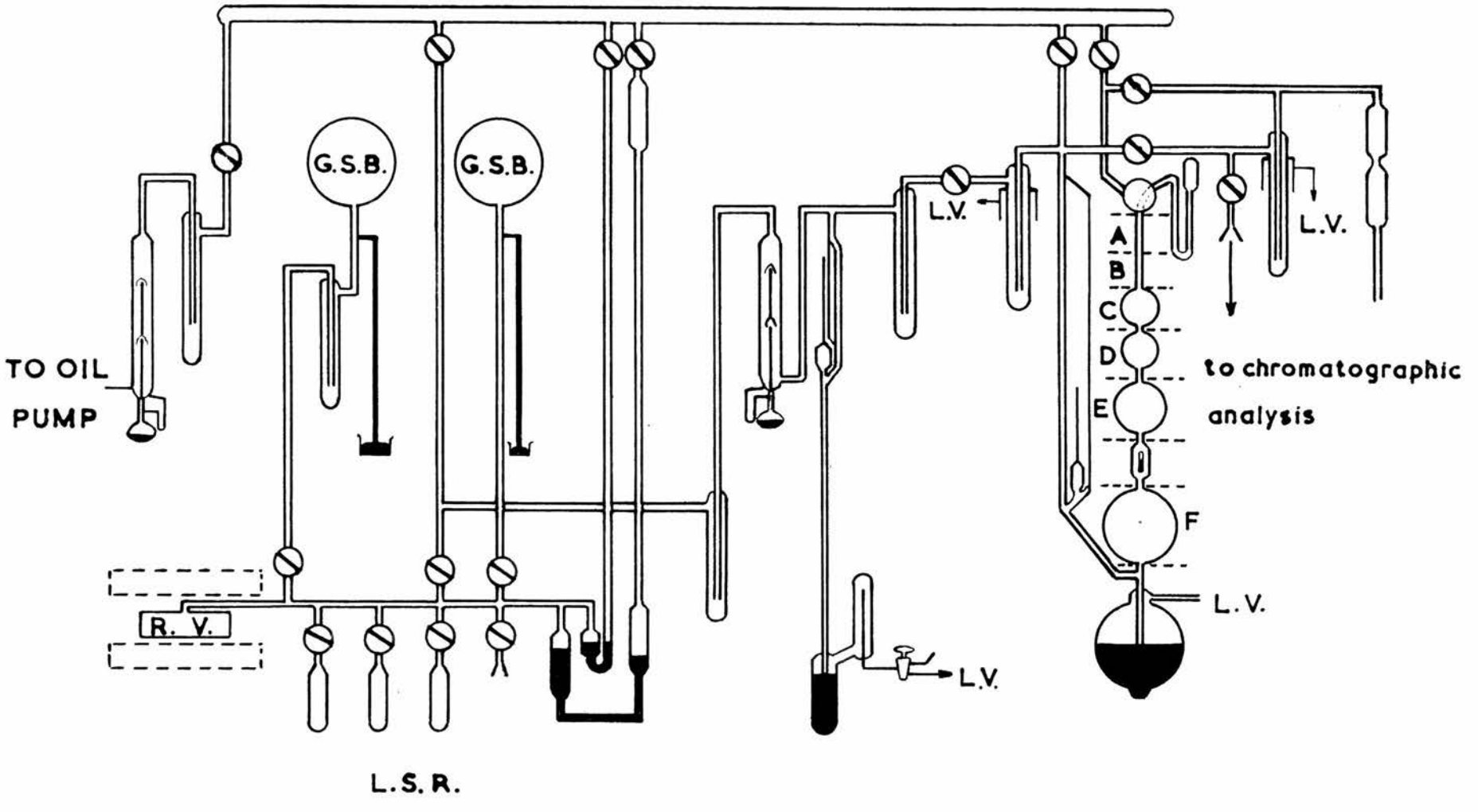


FIG. 2.1.-KINETIC APPARATUS

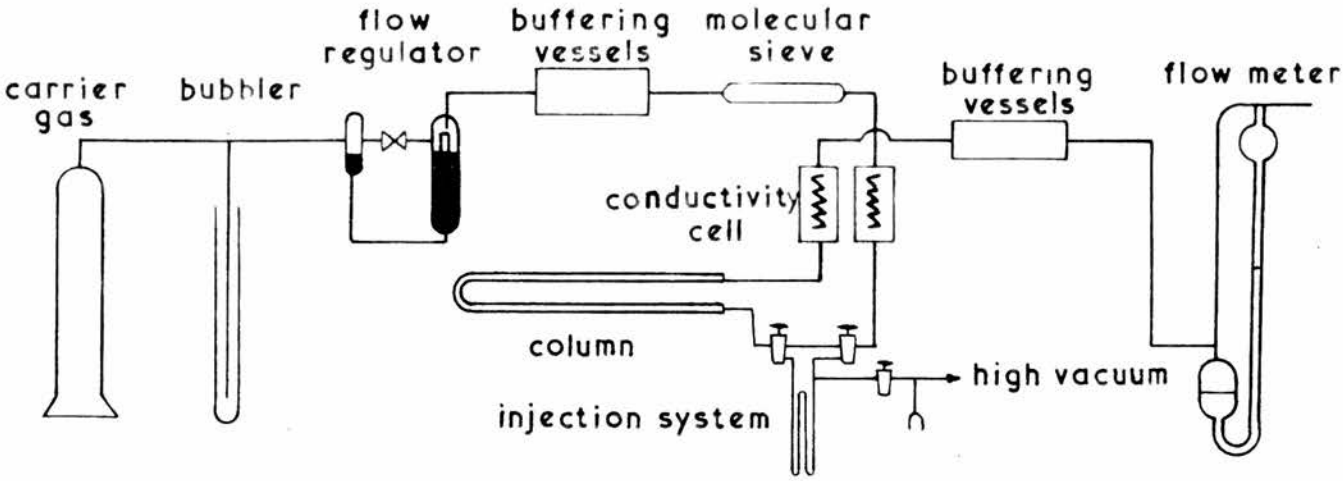


FIG. 2.2.- SCHEMATIC DIAGRAM OF CHROMATOGRAPHY UNIT

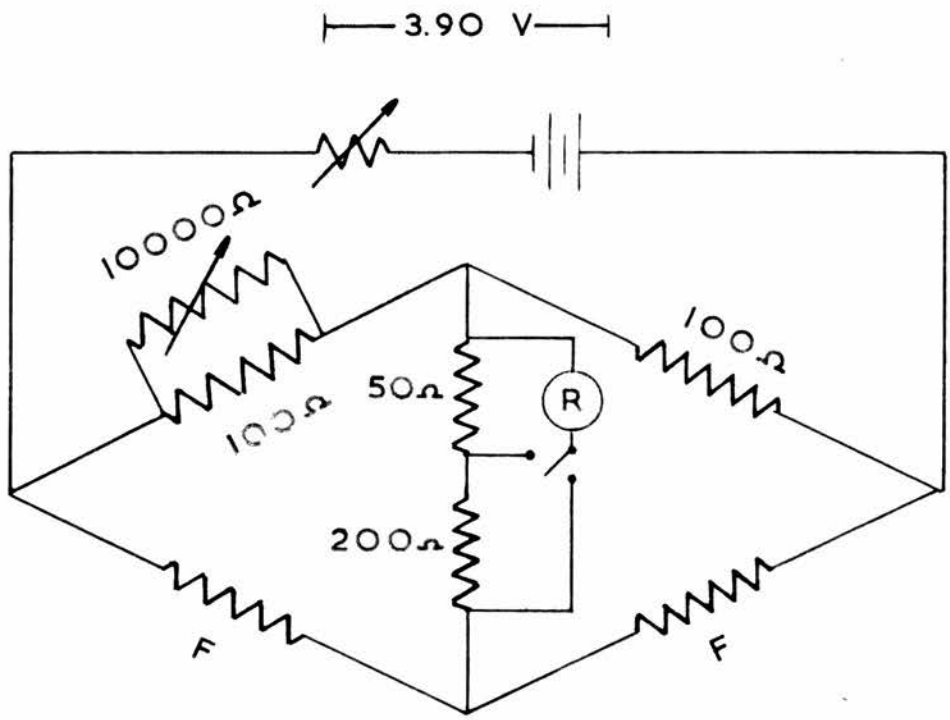


FIG. 2.3.- CIRCUIT FOR CONDUCTIVITY GAUGE

CHAPTER III

THE ADDITION OF METHYL, ETHYL, ISOPROPYL AND t-BUTYL RADICALS TO ACETYLENE AND THE ISOMERIZATION OF ALKENYL RADICALS

Although the addition reactions of radicals to unsaturates have been studied in the past, few determinations of rate constants and Arrhenius parameters for the addition of radicals to acetylenes in the gas phase had been reported at the begining of the present work in 1959. In choosing a system, the photoinitiated chain decomposition of the corresponding aldehyde was selected as source of methyl, ethyl, isopropyl and t-butyl radicals. The advantages of aldehydes as radical sources have been pointed out in part 1. 1.

The radical product of the addition reaction abstracts a hydrogen atom from the aldehydic group to form an olefin which can be directly estimated by analysis. This method is more direct and the determination of the rate constant for the addition involves lower uncertainty than the material balance method used by some workers.

3. 1 EXPERIMENTAL. Materials.- B.D.H. acetaldehyde, propionaldehyde and isobutyraldehyde were purified by bulb-tobulb distillation with rejection of head and tail fractions. Koch trimethylacetaldehyde was purified with the aid of a wide bore gas chromatography apparatus. B.O.G. acetylene was degassed. Materials were shown to be sufficiently pure by gas chromatographyc analysis, before the series of runs was started.

Apparatus.- The kinetic apparatus was essentially the same as described

earlier. Analysis of the products was performed on a column 5 mm I.D. and 10 ft long packed with 40-60 mesh activated alumina poisoned with 1% of squalane. During analysis the temperature was continuously raised from 20 to about 150°C, the rate of increase depending on the nature of the products to be analysed. The flow rate was kept constant at 30 ml/min.

3. 2 CALCULATION OF RESULTS. It has been seen that photolysis of aldehyde RCHO yields a large amount of radicals R. In the presence of acetylene and at temperatures between 100 and 200°C the following reactions among others are expected to occur:

$$RCHO + h\nu \longrightarrow R + \text{other products}$$

$$R + RCHO \longrightarrow RH + RCO \qquad 1$$

$$RCO \longrightarrow R + CO \qquad 1a$$

$$R + R \longrightarrow RR \qquad 2$$

$$R + C_2H_2 \longrightarrow RCH = CH \qquad 3$$

$$RCHCH + RCHO \longrightarrow RCHCH_2 + RCO \qquad 4$$

$$RCO \longrightarrow R + CO \qquad 4a$$

Formyl radicals from the primary photolytic act would decompose to form CO and hydrogen atoms, which would react with either acetylene or aldehyde. In neither eventuality will the presence of atoms seriously complicate the system.

From the reaction scheme it can be shown that

$$R_{RR} = k_2 [R]^2$$

$$R_{CHCH_2} = k_3 [R] [C_2H_2]$$

where R_X represents the rate of formation of X and [Y] is the concentration of Y in the appropiate units. Thus:

$$\frac{k_3}{k_2^{\frac{1}{2}}} = \frac{R_{RCHCH_2}}{R_{RR}^{\frac{1}{2}} [C_2H_2]} \qquad I$$

Conditions were adjusted so that only 2% of the acetylene initially present would react, and addition of the alkenyl radical to acetylene to give, eventually, some diolefin was kept below 3% as far as could be determined by analysis. $[C_2H_2]$ was taken as the initial concentration of acetylene. Reaction 3 and 4 are supposed to be the only ones responsible for the formation of $RCHCH_2$.

Methyl Radicals. When a mixture of acetylene with acetaldehyde was photolysed between 98 and 205°C, at pressures varying between 50 and 80 mmHg and the ratio Acetylen/acetaldehyde from 0.7 to 2.5, ethane and propylene were the main products. In addition, propane and hydrocarbons containing four and five carbon atoms were found at the higher temperatures. Together they amounted to between 1 and 3% of the main products, and were neglected for calculation purposes. No benzene was found though a careful search was made because Drew and Gordon [123] found it when they photolysed acetone in the presence of acetylene between 250 and 500°C.

Results of the runs are summarized in table 3.1. Taking k_2 for the combination of methyl radicals as $\log k_2 = 13.34$ ($mole^{-1}$ cm^3 sec^{-1}) [55] the runs yield

$$k_3 = 10^{11.4} e^{-(7\,700/RT)} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

Ethyl Radicals. Propionaldehyde was photolysed in the presence of acetylene

between 103 and 191°C and at total pressures of 24 to 86 mm Hg. The ratio $[C_2H_2]/[\text{Propionaldehyde}]$ was varied between 0.62 and 3.67. No systematic variations of the points were observed when this ratio was changed.

N-butane and butene-1 were the main products of the reaction. Very small chromatographic peaks that might have been hydrocarbons with five carbon atoms were observed in runs carried out at the higher temperatures. Another peak, whose possition corresponded to that of an unsaturated hydrocarbon of six carbon atoms and which varied irregularly was observed. It was not benzene and its presence could not be easily explained. It was probably some propionaldehyde not completely absorbed.

Table 3. 2 shows the results of the runs. The rate constant was calculated from the rates of formation of n-butane and butene-1. On the assumption that $\log k_2$ (mole^{-1} cm^3 sec^{-1}) = 14.0 for the combination of ethyl radicals, the rate constant for the addition reaction is

$$k_3 = 10^{11.0} \; e^{-(7\,000/RT)} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

Isopropyl radicals. The photolysis of a mixture of isobutyraldehyde and acetylene is expected to yield 3 methyl butene-1 as the only product of addition of isopropyl radical to acetylene. In experiments carried out between 86 and 218°C and at pressures ranging from 22 to 500 mm Hg in the presence and absence of an inert gas, both 3 methyl butene-1, and pentene-1 were detected. The olefins were identified by both their retention times on the chromatographic column and by their infra-red spectra which were compared with those of standard samples. N-propyl radicals were not present in the system as the sample of isobutyraldehyde

used was pure and its photolysis does not yield n-propyl radicals [27,38]. Besides isopropyl radicals do not isomerize at this temperature, as no trace of 2 methyl pentane or n-hexane was detected under conditions in which more than 50% of isomerization would have been needed to explain the results. It was then concluded that the alkenyl radical formed by addition of isopropyl radical to acetylene isomerizes either in its incipient or final form. Accordingly, the calculation of the rate constant was based on equation I' below

$$\frac{k_3}{k_2^{\frac{1}{2}}} = \frac{R_{n\text{-}C_5H_{10}} + R_{i\text{-}C_5H_{10}}}{R^{\frac{1}{2}}_{C_6H_{14}} \; [C_2H_2]} \qquad I'$$

21 runs summarized in table 3.3a give values for the Arrhenius equation for the rate constant of addition. Supposing $\log k_2 = 14.0$ for the combination of isopropyl radicals.

$$k_3 = 10^{11.2} \; e^{-(6\,900/RT)} \; \text{mole}^{-1} \; \text{cm}^3 \; \text{sec}^{-1}$$

between 90 and 204°C, at total pressures varying from 25 to 90 mm Hg and at $[C_2H_2]$ / [isobutyraldehyde] ratios of 0.8 to 4.8.

In an attempt to study the isomerization process, further runs were carried out and results are presented in table 3.3b. The conclusions will be discussed later.

t-butyl radicals. When pivalaldehyde is photolysed in the presence of acetylene, both 3,3 dimethyl butene-1 and 4 methyl pentene-1 are formed. They were identified by both their retention times on the chromatographic column and by their infrar-red spectra, which were compared with those of pure samples. A si-

milar isomerization of the alkenyl radical was postulated to explain the results and calculation of rate constant was made by adding together both olefins.

The analytical system was not suitable for the accurate determination of 2,2,3,3 tetramethyl butane. The concentration of radicals was thus deduced from the rate of formation of isobutene produced by disproportionation of t-butyl radicals, and the ratio of rate constants of disproportionation and combination which was taken as 3.2 (see chapter IV of this thesis). The expression used was

$$\frac{k_3}{k_2^{\frac{1}{2}}} = \frac{R_{C_6H_{12}}(\text{total})}{R^{\frac{1}{2}}_{C_8H_{18}}\,[C_2H_2]} = \frac{R_{C_6H_{12}}(\text{total}) \times 3.2^{\frac{1}{2}}}{R^{\frac{1}{2}}_{C_4H_8}\,[C_2H_2]}$$

$R^{\frac{1}{2}}_{C_4H_8}$ reffers to isobutene formed by disproportionation. However, attack of a radical on the alkyl group of the aldehyde (reaction 6 below) leads to the formation of isobutene. A correction must then be applied to the results of the runs at those temperatures in which such reaction becomes important

$t\text{-}C_4H_9 + t\text{-}C_4H_9 \longrightarrow$	C_8H_{18}		2
$t\text{-}C_4H_9 + t\text{-}C_4H_9 \longrightarrow$	$i\text{-}C_4H_8 + i\text{-}C_4H_{10}$		5
$t\text{-}C_4H_9 + t\text{-}C_4H_9CHO \longrightarrow$	$i\text{-}C_4H_{10} + C_4H_8CHO$		6
$C_4H_8CHO \longrightarrow$	$i\text{-}C_4H_8 + CHO$		6a

It can be seen that

$$R_{C_4H_8}(5) = R_{C_4H_8}(\text{total}) \times (1\text{-}X) = k_5\,[C_4H_9]^2$$

$$R_{C_4H_8}(6a) = R_{C_4H_8}(\text{total}) \times X = k_6\,[C_4H_9]\,[\text{Ald}]$$

thus,

$$\frac{k_6}{k_5^{1/5}} = \frac{k_6}{(3.2\ k_2)^{\frac{1}{2}}} = \frac{R_{C_4H_8}\ (\text{total}) \times X}{R^{\frac{1}{2}}_{C_4H_8}\ (\text{total}) \times (1-X)^{\frac{1}{2}}\ [\text{Ald}]}$$

and as $k_6/k_2^{\frac{1}{2}}$ is known after Birrell and Trotman-Dickenson [28], the percentage of isobutene formed by disproportionation can be calculated for each run.

Results of the runs carried out between 100 and 223°C are summarized in table 3.4. The pressure was varied between 20 and 350 mm Hg, but in most runs the pressure was below 100 mm Hg. Withing this range, the ratio acetylene/pivalaldehyde varied from 0.21 to 5.5, with two higher values of 16 and 7.5.

The rate constant for the addition reaction is given by

$$k_3 = 10^{10.7}\ e^{-(5.400/RT)}\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

on the assumption that $\log k_2 = 14.0$ for the combination of t-butyl radicals.

Arrhenius plots for the four addition reactions are shown in fig. 3.1.

The isomerization of alkenyl radicals. At high temperatures, isomerization of the radical formed when t-butyl radical adds to acetylene does not take place, and only 5% of the radical from isopropyl isomerizes to give pentene-1. The extent of isomerization is gradually reduced when increasing pressures of nitrogen are added to a constant pressure of reactants, although the relative efficiency is, as would have been expected from such a small molecule, low. Reduction of the total pressure leads to 4 methyl pentene-1 and pentene-1 respectively in the products. The rate of isomerization was unaltered when isopropyl ra-

dicals were produced by photolysis of isobutyraldehyde with light filtered through a sheet of pyrex glass. Tables 3.3b and 3.4 and fig. 3.2 show the effect of pressure on the isomerization and how this effect is independent of the reactivity of the gases present in the system, as far as it could be shown under the present conditions.

From results of experiments carried out at low pressure over a range of temperatures, plots of the logarithms of the ratios pentene-1/3 methyl butene-1 and 4 methyl pentene-1/3,3 dimethyl butene-1 against the reciprocal of the absolute temperature showed greater isomerization at higher temperatures. The isopropyl plots flattened out at the low temperatures as would have been expected if most of the energy for isomerization came from the exothermicity of the addition reaction.

Although experiments were not very accurate and the results are not conclusive, it could be observed that for each radical and at the higher temperatures, approximately parallel straight lines could be drawn through points corresponding to runs carried out at the same pressure, as may be seen in figs. 3.3 and 3.4.

Notes on Tables 3.1, 3.2, 3.3a, 3.3b and 3.4

All products are in rates of formation of 10^{12} mole cm^{-3} sec^{-1}, and all subsequent calculation involve these units.

C_2H_2 refers to the initial concentration of acetylene - 10^6.mole cm^{-3}

Ald refers to the concentration of the corresponding aldehyde - 10^6 mole cm^{-3}

$k_3/k_2^{\frac{1}{2}}$ is given in $mole^{-\frac{1}{2}}$ $cm^{3/2}$ $sec^{-\frac{1}{2}}$

C_2H_6 - ethane

C_3H_6 - propylene

$n\text{-}C_4H_8$ - butene-1

$n\text{-}C_4H_{10}$ - n-butane

$i\text{-}C_4H_8tot$ - total amount of isobutene, in table 3.4

$i\text{-}C_4H_8disp$ - isobutene formed by disproportionation

$i\text{-}C_4H_8abs$ - isobutene formed by attack of t-butyl radicals on pivalaldehyde

$i\text{-}C_5H_{10}$ - 3 methyl butene-1

$n\text{-}C_5H_{10}$ - pentene-1

C_6H_{14} - 2,3, dimethyl butane

$Me_2C_4H_6$ - 3,3 dimethyl butene-1

MeC_5H_9 - 4 methyl pentene-1

% H abs - percentage of isobutene formed by attack of t-butyl radicals on pivalaldehyde.

P - Light filtered through a sheet of pyrex glass

P_X - Pressure in mm Hg of compound X

TABLE 3. 1 ADDITION OF METHYL RADICALS TO ACETYLENE

RUN	$T^{o}K$	t	C_2H_2	$\frac{C_2H_2}{Ald}$	$R_{C_2H_6}$	$R_{C_3H_6}$	$\log k_3/k_2^{\frac{1}{2}}$
29	370.8	900	1.275	2.119	7.534	5.336	0.1831
30	375	900	1.774	2.468	8.474	8.16	0.1987
31	376	1800	1.945	1.647	11.75	10.83	0.2102
42	378.6	1080	2.136	1.968	32.44	18.83	0.1898
36	385.2	900	2.329	2.507	10.67	17.56	0.3638
41	385.6	900	1.787	1.773	38.93	19.46	0.2420
37	395.5	900	1.274	0.957	18.52	17.80	0.4391
20	410.4	900	1.362	2.456	12.24	16.63	0.5429
22	411.2	720	1.988	1.762	17.66	35.31	0.6259
21	413.5	900	1.245	0.971	24.63	25.11	0.5840
27	430.8	900	1.001	0.9427	17.58	25.74	0.7836
26	431	900	0.928	1.547	10.05	17.89	0.7842
23	433.2	1800	0.5151	1.02	9.73	8.789	0.7379
24	434	960	1.334	1.658	13.53	29.72	0.7822
25	434.5	900	1.536	2.455	6.592	29.2	0.8695
28	434.5	1200	0.8644	0.691	18.32	23.54	0.8026
32	458.5	1020	0.6456	0.7836	12.46	24.92	1.0388
39	478.8	900	1.869	1.688	14.75	107.3	1.1747

TABLE 3. 2 ADDITION OF ETHYL RADICALS TO ACETYLENE

RUN	T°K	t	C_2H_2	$\frac{C_2H_2}{Ald}$	$R_{n-C_4H_{10}}$	$R_{n-C_4H_8}$	$\log k_3/k_2^{\frac{1}{2}}$
61	376.5	900	1.770	2.845	25.41	7.623	I'9315
62	378.2	900	1.727	1.817	40.32	9.623	I'9433
65	386.3	960	1.090	1.779	22.87	5.399	0.0154
46	399.9	900	0.8249	1.330	33.21	5.591	0.0705
47	402.7	1020	1.176	1.613	40.65	10.16	0.1322
48	403.6	900	1.382	2.552	29.82	10.51	0.1440
49	406.6	900	1.819	2.334	48.54	21.24	0.2294
63	412.6	900	0.7335	0.6187	44.72	8.808	0.2542
64	416.5	960	1.693	2.818	20.65	16.36	0.3275
55	424.8	900	0.8680	0.7570	47.43	18.30	0.4858
53	425.7	900	1.304	2.465	21.69	14.56	0.3800
54	429.0	900	1.337	1.279	34.89	22.70	0.4587
45	444.7	1020	0.9874	1.485	29.29	18.18	0.5316
44	447.0	900	2.433	3.593	21.01	38.69	0.5403
51	457.8	900	1.202	2.574	12.20	18.63	0.6460
58	459.7	1260	1.653	3.670	7.259	18.88	0.6272
50	460.0	900	0.8754	1.100	30.83	25.23	0.7153
52	460.4	1020	1.527	2.835	13.75	23.56	0.6191
56	462.0	900	1.128	2.462	11.86	16.61	0.6310
57	464.1	900	0.5147	0.9545	19.32	10.51	0.6668

TABLE 3.3a ADDITION OF ISOPROPYL RADICALS TO ACETYLENE

RUN	T°K	t	C_2H_2	$\frac{C_2H_2}{Ald}$	$R_{i-C_5H_{10}}$	$R_{n-C_5H_{10}}$	$R_{C_6H_{14}}$	$\log k_3/k_2^{\frac{1}{2}}$
90	372.1	900	,0.8184	1.040	2.304	0.7454	8.132	.1188
91	373.5	900	1.486	2.050	4.404	1.355	8.132	.1332
81	375.7	900	0.7509	0.9539	2.507	1.016	9.961	.1721
92	383	900	1.889	2.944	7.047	2.032	6.234	.2844
93	385.5	900	0.8674	1.089	3.524	1.559	8.132	.3129
75	386.5	600	1.342	1.754	7.011	2.032	9.247	.3456
71	409.75	900	1.360	1.900	10.09	3.795	7.521	.5708
72	409.75	900	1.693	2.243	12.27	4.066	7.115	.5582
69	411.5	900	1.521	2.166	12.06	4.743	7.318	.6112
70	411.8	900	0.5916	0.7986	3.524	2.237	8.945	.5129
66	412.5	900	0.5571	0.7214	2.914	2.169	9.283	.4764
80	412.9	600	2.000	1.558	22.36	6.198	11.69	.6207
79	414.8	900	2.117	2.946	16.27	4.743	6.776	.5812
96	415.5	900	0.5202	1.010	1.693	1.627	4.133	.4967
76	430.7	900	1.077	1.457	9.690	5.218	6.911	.7212
83	447.1	900	1.261	2.122	14.43	7.658	4.472	.9177
82	448	900	0.5281	0.7938	4.133	4.608	5.489	.8490
73	450.5	900	0.8786	1.328	7.521	6.640	4.540	.8786
74	461.6	600	1.927	2.697	20.93	10.57	3.862	.9200
78	470.1	720	1.631	2.407	15.92	11.01	3.304	.9584
77	470.2	900	0.6146	0.9270	5.353	7.454	5.150	.9629

TABLE 3.3b ADDITION OF ISOPROPYL RADICALS TO ACETYLENE

RUN	T°K	t	C_2H_2	Ald	$R_{i-C_5H_{10}}$	$R_{n-C_5H_{10}}$	$R_{C_6H_{14}}$	$\frac{R_{n-C_5H_{10}}}{R_{i-C_5H_{10}}}$	$P_{C_2H_2}$	P_{Ald}	$P_{in.gas}$	Tot.P	$\log k_3/k_2^{\frac{1}{2}}$
164	359.9	1200	1.729	.432	3.354	1.220	10.73	.3637	38.79	9.70	-	48.49	$\bar{1}$.9073
161	360.6	1800	2.137	.458	4.370	1.228	10.54	.2798	48.04	10.27	-	58.31	$\bar{1}$.9062
151	371.9	1800	1.891	.6112	3.253	1.016	4.098	.3125	43.85	14.36	-	58.21	.0472
153	372.2	3600	1.286	.8166	3.540	1.220	12.03	.3429	29.84	18.94	-	48.78	.0283
154	374.4	3600	1.700	.8052	4.912	1.728	13.80	.3505	39.68	18.74	-	58.47	.0217
152	375.7	1800	1.242	.8279	2.745	.915	5.928	.3333	29.09	19.39	-	48.48	.0827
127	376.2	600	1.666	.7311	11.90	3.659	36.59	.3077	40.14	17.60	-	57.74	.1881
126	390.3	900	1.205	.7371	8.539	3.253	35.24	.3572	30.73	18.79	-	49.52	.2170
150	401.1	1200	.8112	.7577	7.318	3.354	19.87	.4583	20.29	18.94	23.86	63.09	.4700
141	402.6	120	8.328	5.671	263.7	15.24	96.56	.057	209.	142.	-	351.	.5157
149	403.0	1200	.8489	.7362	7.164	3.405	19.72	.4784	21.33	18.49	29.40	69.22	.4478
140	403.8	1800	.7762	.3081	1.321	1.422	7.148	1.076	19.54	7.76	-	26.30	.1213
148	404.2	1200	.7874	.7459	5.487	2.897	17.43	.5278	19.85	18.79	10.29	48.93	.4066
137	404.0	120	5.201	4.208	124.6	9.147	103.1	.073	131.	106.	-	237.	.4031
145	404.9	900	.8863	.6972	10.77	1.627	22.43	.1510	22.38	17.60	310.0	351.	.4705
134	405.4	180	5.024	2.394	113.5	10.16	54.20	.089	127.0	60.5	-	187.5	.5299
135	405.4	900	1.600	.7259	14.78	5.285	25.07	.3562	40.42	19.85	-	60.27	.3987
159	405.7	900	1.103	.4305	6.302	3.253	11.25	.5220	27.89	10.89	-	38.78	.4121
142	405.9	1200	.8074	.7427	8.943	1.829	21.96	.2033	20.44	18.79	211.0	252.	.4565
146	406.5	900	.7889	.7595	7.318	2.440	21.62	.3333	19.99	19.24	87.	126.	.4250
144	407.0	900	.8054	.7173	5.828	3.253	18.63	.5517	20.44	18.20	21.18	59.82	.4201
138	407.6	1200	.5225	.3640	1.321	1.524	11.74	1.177	13.27	9.25	-	22.52	.2013
143	408.5	900	.8435	.6969	7.318	3.253	19.32	.4440	21.49	17.75	41.	80.24	.4551
132	408.6	600	.6383	.8900	7.011	3.659	33.13	.5000	16.26	22.38	-	38.93	.4631
139	408.6	900	1.932	1.001	18.50	4.878	28.12	.2637	49.22	25.51	-	74.73	.3584
124	408.6	600	.7886	.7304	18.60	2.439	37.40	.1311	20.14	18.65	461.	499.8	.6397
147	408.9	900	.7966	.7372	5.396	2.845	18.03	.5184	20.29	18.79	-	39.08	.3887
136	409.8	900	.8170	.6831	4.878	3.253	22.53	.6667	20.88	17.46	-	38.34	.3211
131	410.9	900	1.177	.705	10.37	5.285	25.14	.5098	30.14	18.05	-	48.19	.4238
155	412.7	60	12.01	7.484	484.8	18.29	58.93	.048	310.	193	-	503.00	.7365
133	413.2	360	2.426	1.505	57.93	13.21	54.04	.2281	62.5	38.79	-	101.29	.5977
129	452.5	600	.709	1.031	15.24	13.52	34.04	.8800	19.99	29.01	-	49.04	.8408
128	452.9	900	1.253	.475	9.353	9.010	10.71	.9565	35.21	13.43	-	48.64	.6518
130	454.1	900	1.428	.638	16.81	13.01	13.55	.7711	40.42	18.05	-	58.47	.7518
123	475.8	2400	1.252	.7591	4.116	3.583	.330	.8704	37.15	22.53	-	59.68	.9293
125	488.2	9600	.6714	.9215	9.845	15.44	20.01	1.558	20.44	28.05	-	48.49	.9108
162P	383.4	3600	1.142	.9048	1.627	.559	.9995	.3439	27.30	21.64	-	48.94	.2819
156P	412.3	3600	1.184	.7487	2.439	1.067	.6267	.4375	30.43	19.24	-	49.67	.5730
160P	436.7	3600	1.046	.7561	2.134	1.372	.3388	.6430	28.49	20.54	-	49.03	.7602
157P	450.7	3600	.7857	.9716	2.625	2.084	.3727	.7884	22.08	27.30	-	49.38	.9935
163P	491.1	3600	.5454	1.052	2.337	3.706	.2541	1.587	16.70	32.22	-	48.92	1.3422

TABLE 3.4 ADDITION OF t-BUTYL RADICALS TO ACETYLENE

RUN	$T^{o}K$	t	C_2H_2	Ald	$R_{C_4H_8}$ tot.	$R_{C_4H_8}$ disp	$\frac{R_{C_4H_8}}{H\ abst.}$	% H abst	$R_{Me_2C_4H_6}$	$R_{Me\ C_5H_9}$	$P_{C_2H_2}$	P_{Ald}	Tot.P	$\frac{R_{Me\ C_5H_9}}{R_{Me_2C_4H_6}}$	$\log k_3/k_2^{\frac{1}{2}}$
122	373.2	3600	1.567	.9510	3.913	3.913	-	-	5.455	.627	36.45	22.13	58.58	.1143	.6135
100	388.1	3600	.6918	1.431	5.590	5.590	-	-	3.727	.5929	16.74	34.61	51.35	.1579	.7425
97	398.2	6000	.6570	0.9770	3.892	3.892	-	-	3.526	.9145	16.31	24.25	40.56	.2583	.8556
115	405.6	600	13.09	.7964	.7114	.6089	.1024	14.4	28.050	-	331.	20.14	351.14	.0	.7550
113	408.2	900	6.915	.7912	2.237	2.034	.2012	9.0	21.20	.7793	176.	20.14	196.14	.0368	.6946
117	408.8	1800	.8193	1.551	4.539	3.972	.5674	12.5	6.166	1.253	20.88	39.53	60.41	.2025	.9762
116	409.4	3600	1.596	.7482	2.541	2.328	.2136	8.4	5.455	1.016	40.65	19.09	59.74	.1858	.7426
111	410.0	900	3.052	.7762	2.982	2.839	.1431	4.8	14.90	1.898	78.0	19.84	97.84	.1263	.8449
107	410.2	4500	1.201	1.027	4.390	3.999	.3907	8.9	6.769	1.314	30.73	26.25	56.98	.1935	.8440
109	410.6	3600	.594	.927	4.167	3.817	.3500	8.4	3.794	1.203	15.22	23.72	38.94	.3196	.9469
106	411.3	3600	1.400	.520	1.060	.9596	.1007	9.5	3.794	.8486	35.88	13.33	49.21	.2268	.8727
112	411.4	1200	2.356	.768	2.237	2.019	.2170	9.7	10.57	1.626	60.42	19.69	80.11	.1555	.8797
108	412.4	4500	.766	.754	2.371	2.146	.2253	9.5	3.171	.935	19.69	19.39	39.08	.2770	.8758
114	412.4	3600	.383	.778	3.489	3.203	.2862	8.2	1.636	.935	9.85	19.99	29.84	.5715	.8931
118	413.0	3600	1.981	.359	.4912	.4401	.0511	10.4	2.152	.4743	51.05	9.27	60.32	.2182	.6176
110	413.8	3600	.399	.370	1.863	1.759	.1043	5.6	.695	.745	10.29	9.55	19.84	1.055	.7540
119	414.0	2400	.3987	1.907	7.852	6.784	1.068	13.6	2.237	.584	10.41	49.22	59.63	.2631	.7504
98	415.7	5400	.832	1.100	3.444	3.014	.4305	12.5	4.754	1.152	21.56	28.51	50.07	.2404	.9304
105	417.1	3600	.420	.693	3.659	3.359	.3000	8.2	1.728	1.135	10.92	18.01	28.93	.6591	.8887
99	447.2	3600	1.4600	1.149	2.117	1.404	.6972	33.7	8.876	2.320	40.70	31.77	72.47	.2588	1.1235
102	455.0	5400	.865	.830	1.660	1.170	.4897	29.5	3.253	2.021	24.53	23.55	48.08	.6240	1.0759
101	456.7	3600	.413	1.086	4.032	2.552	1.480	36.7	2.422	2.457	11.77	30.92	42.69	1.014	1.1456
104	462.3	3600	1.117	.965	2.032	1.193	.8397	41.3	4.285	2.457	32.20	27.81	60.01	.5727	1.0443
120	482.5	1800	.669	1.329	4.979	2.365	2.614	52.5	4.676	6.471	30.14	39.98	60.12	1.380	1.3124
121	481.1	3600	.373	.622	a.f.	a.f.	a.f.	-	.539	1.948	11.19	18.68	29.87	3.572	-
103	496.3	4500	.481	.990	2.819	1.057	1.762	62.5	1.965	4.296	30.64	14.89	45.53	2.191	1.3952

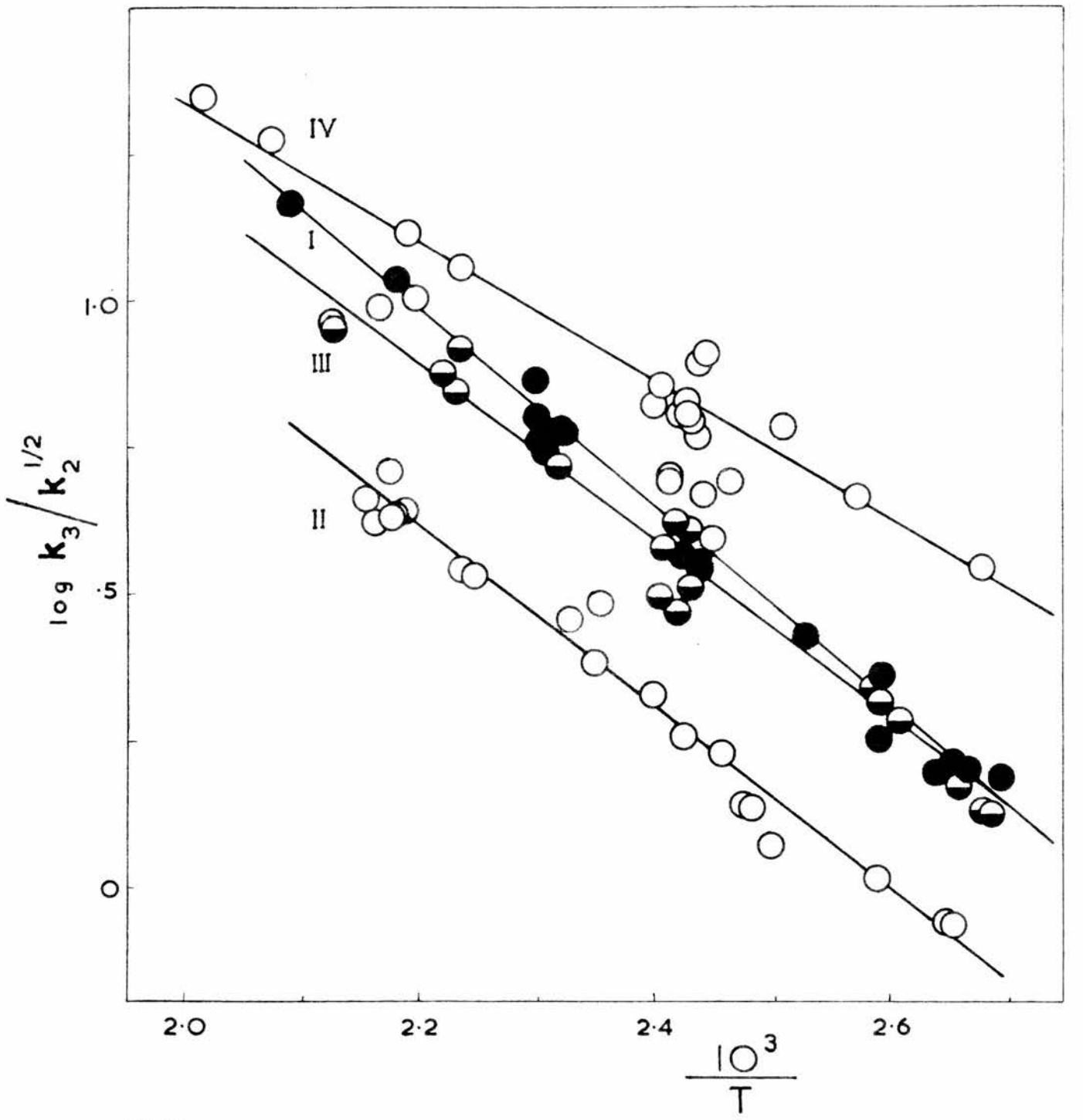


FIG. 3-1 Arrhenius plots for the addition of radicals to acetylene

I. Methyl radicals
II. Ethyl radicals
III. Isopropyl radicals
IV. t-butyl radicals

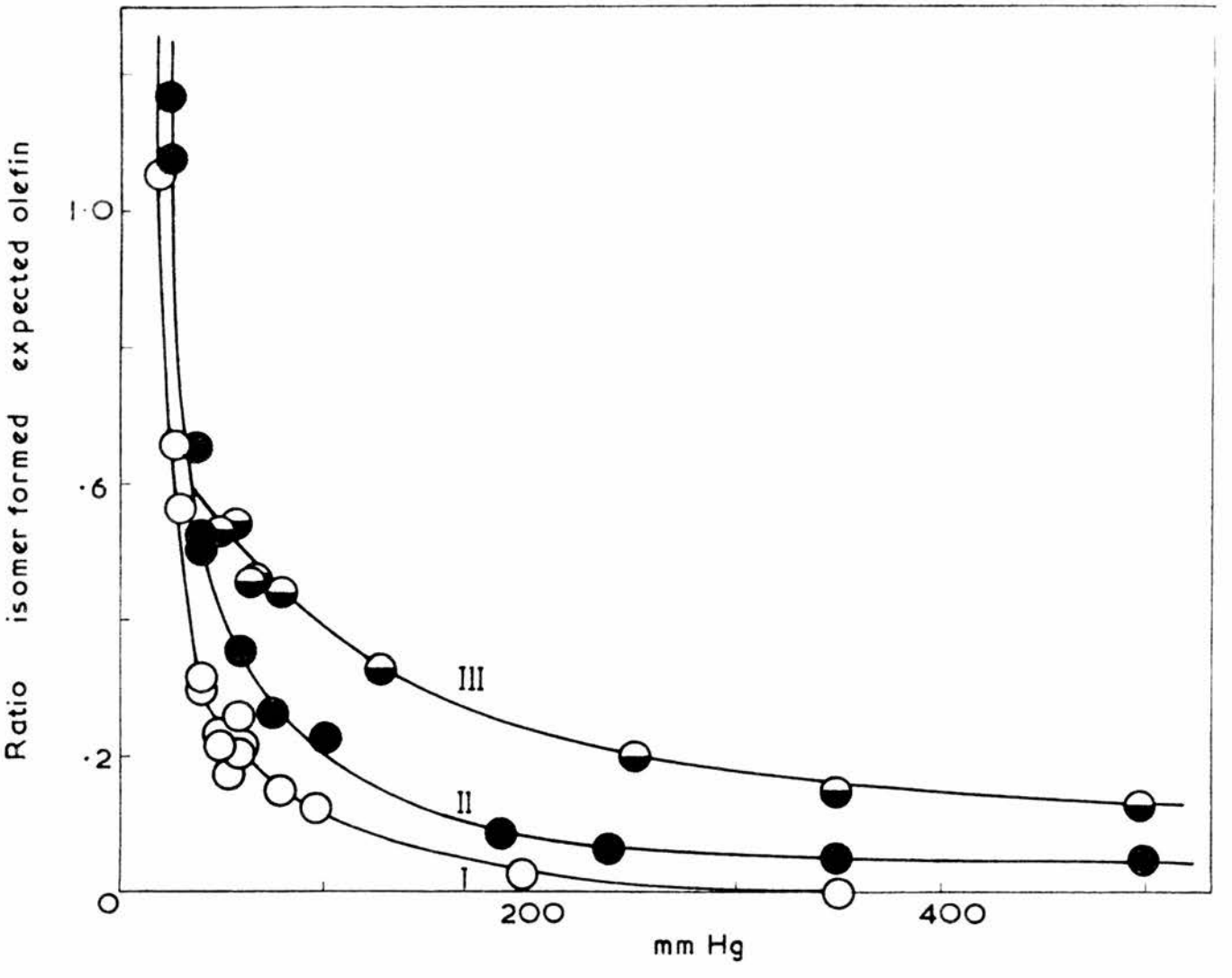


FIG. 3-2 Dependance of isomerization on total pressure

I. t-butyl/ acetylene system

II. isopropyl / acetylene system

III. isopropyl / acetylene in the presence of inert gas

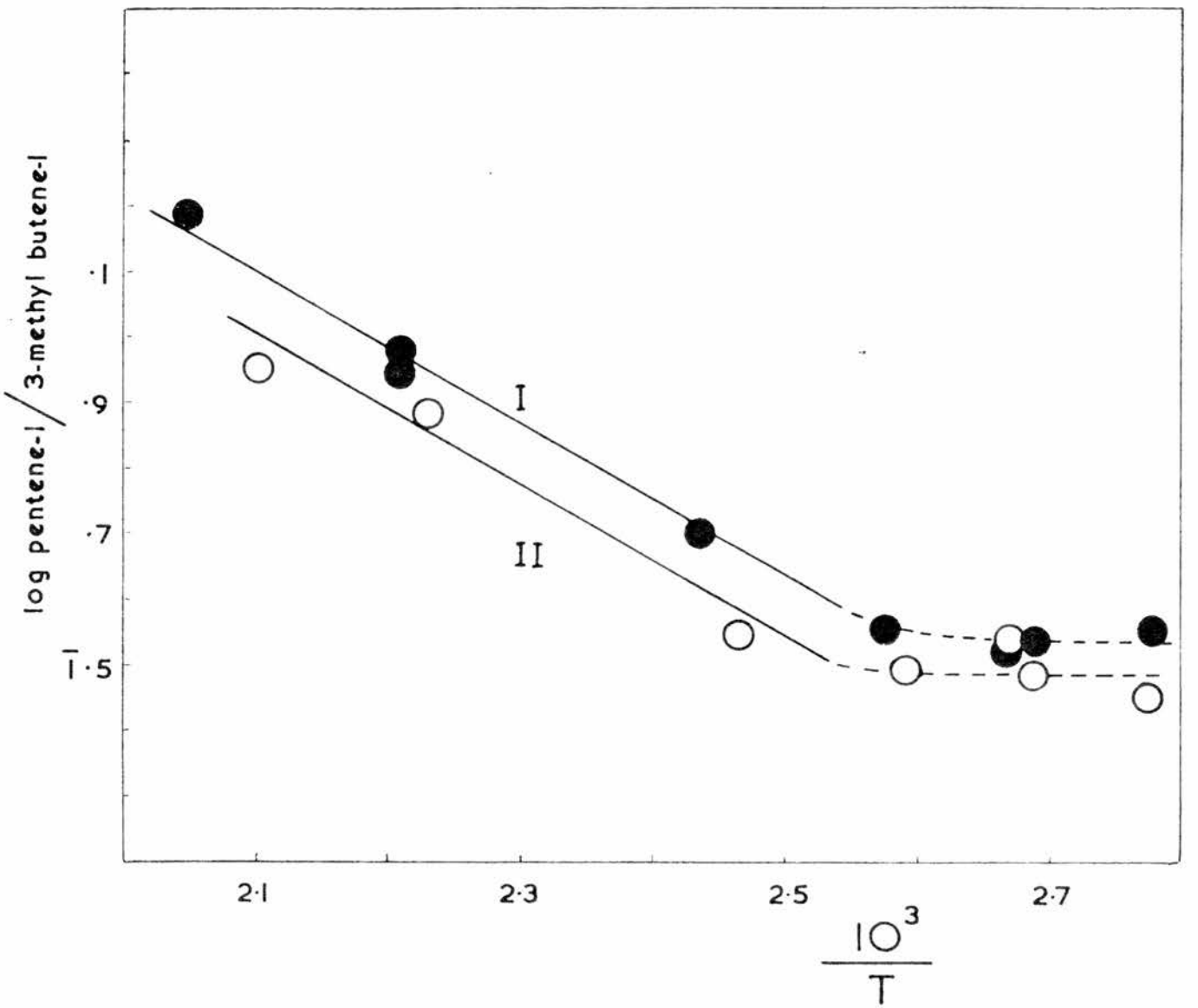


FIG. 3-3 Temperature coefficient for the isomerization of alkenyl radicals ; isopropyl / acetylene

I. 50 mm Hg

II. 60 mm Hg

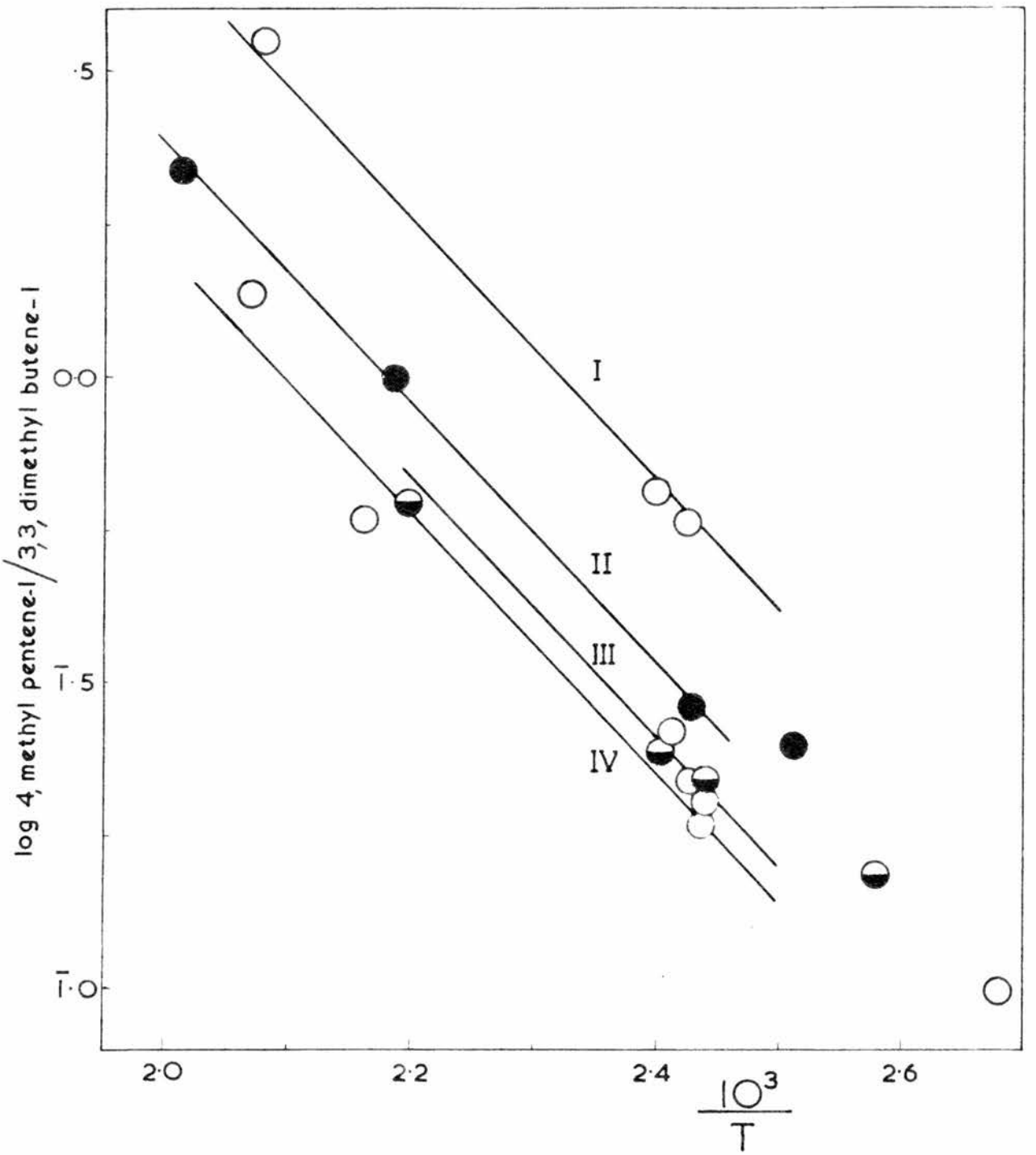


FIG. 3-4.– Temperature coefficient for isomerization of alkenyl radicals : t-butyl/ acetylene.

I 30 mm. Hg.– II 40 mm Hg.– III 50 mm.– IV 60 mm

CHAPTER IV

THE DISPROPORTIONATION OF t-BUTYL RADICALS AND THEIR REACTIONS WITH ETHYL AND ISOPROPYL RADICALS

The only values reported for the ratio of rates of crossdisproportionation and crossccombination of t-butyl radicals with ethyl and isopropyl have been deduced from the results of experiments in which the radicals were produced by photosensitized hydrogenation of olefins. It was considered convenient to calculate the crossdisproportionation ratios from studies of systems in which the radicals are believed to be formed in thermal equilibrium with their environment. Thus the photolysis of the corresponding dialkyl ketones was selected as the best and cleanest radical source available.

As no temperature coefficient is expected in this type of reaction, experiments were all carried out at the same temperature.

Although values of $\Delta(Bu^t, Bu^t)$ have been reported in the past, the ratio was recalculated using both di-t-butyl ketone and trimethylacetaldehyde as photolytic sources of t-butyl radicals.

4. 1 EXPERIMENTAL. Materials.- B.D.H. diethyl ketone was purified by bulb to bulb distillation with rejection of head and tail fractions. Diisopropyl ketone was a sample from Shell Chemicals; it was distilled. Di-t-butyl ketone was prepared by condensing t-butyl chloride and methyl pivalate over sodium sand and oxidizing the resultant mixture of ketone and alcohol with concentrated nitric acid according to the method of Bartlett and Schneider [129] and was carefully

distilled. Koch pivalaldehyde was purified by wide bore gas chromatography. All samples were shown to be pure by gas chromatography and by the identity of the products of their photolyses.

Apparatus. It was essentially the same as described in chapter II. Absorbents for acetylene and aldehyde were removed and all tubing connecting the reaction vessel with the tapped container where products of the reaction were stored for analysis, was kept at about 100°C to avoid condensation of unreacted ketone or octane. In some of the runs, the aluminium foil reflector was removed. No difference was observed in the results.

Two chromatographic columns were used for analysis; both were packed with 40-60 mesh activated alumina impregnated with 3% of squalane. The second one could either be bypassed or inserted in the gas stream. The flow rate was kept constant at 30 ml/minute and the temperature of the columns was gradually increased. Analysis of products was carried out as follows:

Ethyl, t-butyl system.- Both columns were 5 ft long each and were inserted in the flow until ethane and ethylene had been eluted. This gave a good separation of these light hydrocarbons. When the peak corresponding to ethylene had appeared on the chromatogram, the second column was bypassed and only the first one was used which was sufficient to separate the fraction containing hydrocarbons with four carbon atoms. With this agrangement, a fairly narrow peak was obtained for 2,2,3,3, tetramethylbutane, which could thus be directly measured.

Isopropyl, t-butyl system.- The second column was 2 ft long and was inserted in the flow in those cases in which the rate of formation of propylene had to be determined. Measurement of isobutene, hexane, heptane and octane could

easily be carried out with the first column only, which was 5 ft long.

4. 2 CALCULATION OF RESULTS. No temperature coefficient is expected when calculating disproportionation ratios. The work presented here was carried out at 77 ± 5°C. This temperature is sufficiently high to allow a reasonable pressure of reactants and at the same time low enough for hydrogen abstraction reactions by radicals to be unimportant.

The disproportionation of t-butyl radicals. Di-t-butyl ketone was photolysed at pressures from 2.4 to 12 mm Hg and the rates of formation of isobutane, isobutene and 2,2,3,3 tetramethylbutane (C_8H_{18}) determined. The light was filtered through a sheet of pyrex glass 1 mm thick in some of the runs. Pivalaldehyde was also photolysed at pressures of 12 to 50 mm Hg and rates of formation of isobutene and octane measured.

Results of the runs are presented in table 4.1. The average value for the ratio of the rate constants of disproportionation and combination, based on the determination of isobutene is

$$\Delta(Bu^t, Bu^t) = 3.185$$

Measurements of the rate of formation of isobutane yield a value of 3.161, in excellent agreement, although the first one is to be preferred and was used in all subsequent calculations.

Ethyl and t-butyl radicals, produced in the photolysis of the corresponding dialkyl ketones undergo the following reactions:

$$2\ C_2H_5 \longrightarrow nC_4H_{10} \quad 1$$
$$\longrightarrow C_2H_4 + C_2H_6 \quad 2$$
$$C_2H_5 + t\text{-}C_4H_9 \longrightarrow C_6H_{14} \quad 3$$
$$\longrightarrow C_2H_6 + i\text{-}C_4H_8 \quad 4$$

$$\longrightarrow \quad C_2H_4 + i\text{-}C_4H_{10} \qquad 5$$

$$2\ t\text{-}C_4H_9 \longrightarrow \quad C_8H_{18} \qquad 6$$

$$\longrightarrow \quad i\text{-}C_4H_{10} + i\text{-}C_4H_8 \qquad 7$$

Other reactions such as hydrogen abstraction by a radical from the ketones or addition to the olefin produced are negligible at this temperature and low conversion. Decomposition does not occur at all. Reactions 1 to 7 are supposed to be the only sources of ethane, ethylene, n and iso-butane, isobutene, 2,2 dimethyl butane and 2,2,3,3 tetramethyl butane.

From the above scheme

$$R_{iC_4H_8} = k_4 [C_2H_5][C_4H_9] + k_7 [C_4H_9]^2 \qquad I$$

$$R_{C_6H_{14}} = k_3 [C_2H_5][C_4H_9] \qquad II$$

and

$$\Delta(Et, Bu^t) = \frac{k_4}{k_3} = \frac{R_{iC_4H_8} - k_7 [C_4H_9]^2}{R_{C_6H_{14}}} \qquad III$$

where R_X is the rate of formation of X and k_7 the rate constant of reaction 7.

$k_7 [C_4H_9]^2$ which is equal to the rate of formation of isobutene by reaction 7 can be easily evaluated from the rate of formation of octane and the ratio

$$\frac{k_7}{k_6} = \frac{R_{iC_4H_8}(7)}{R_{C_8H_{18}}}$$

which has been previously found

$$k_7 [C_4H_9]^2 = R_{iC_4H_8}(7) = 3.185\ R_{C_8H_{18}} \qquad IV$$

and the required ratio of rate constants from

$$\Delta(Et,\ Bu^t) = \frac{R_{iC_4H_8} - 3.185R_{C_8H_{18}}}{R_{C_6H_{14}}} \qquad \text{IIIa}$$

Similarly

$$\Delta(Bu^t,\ Et) = \frac{k_5}{k_3} = \frac{R_{C_2H_4} - 0.15R_{nC_4H_{10}}}{R_{C_6H_{14}}} \qquad \text{V}$$

Excess of diethyl ketone reduces the size of the second term in the numerator of formula IIIa, and excess of di-t-butyl ketone reduces the size of the corresponding term in equation V. Two series of runs were carried out in which one of the ketones was, in turn, in excess. Hence, small errors in the determination of autodisproportionation ratios had little effect on the final result.

Whenever possible, rates of formation were directly measured. However, excess of one ketone brought about a parallel decrease in the size of the chromatographic peak corresponding to the dimer of the radical produced from the other ketone, and its direct determination could not be done with accuracy. In some of the runs, then, it was calculated as follows: It can be seen that

$$k_3/(k_1 \times k_6)^{\frac{1}{2}} = R_{C_6H_{14}}/(R_{nC_4H_{10}} \times R_{C_8H_{18}})^{\frac{1}{2}} \qquad \text{VI}$$

According to the simple collision theory of chemical kinetics, this ratio may be taken as 2 and the most reliable experimental determinations approximate closely to this figure (see table 1.1). Hence

$$R_{C_8H_{18}} = \frac{R^2_{C_6H_{14}}}{4 \times R_{nC_4H_{10}}} \qquad \text{VIa}$$

and

$$R_{nC_4H_{10}} = \frac{R^2_{C_6H_{14}}}{4 \times R_{C_8H_{18}}} \qquad \text{VIb}$$

The values obtained from the results of the runs and summarized in table 4.2 using equations IIIa and V are:

$$\Delta(Et,\ Bu^t) = 0.48$$

at pressures from 17 to 45 mm Hg.

$$\Delta(Bu^t,\ Et) = 0.31$$

at pressures of 7 to 16 mm Hg.

A check may be done on those values. Reaction 4 produces ethane and isobutene in equal amounts. Ethane is also produced by reaction 2, and it can be shown that instead of equation IIIa, the following expression may be used

$$\Delta(Et,\ Bu^t) = \frac{R_{C_2H_6} - 0.15R_{nC_4H_{10}}}{R_{C_6H_{14}}} \qquad \text{VII}$$

The chromatographic peak corresponding to C_2H_6 was rather narrow and its accurate measurement difficult. The value of 0.53 obtained from equation VII is nevertheless in good agreement with the value deduced using expression IIIa. An evaluation of $\Delta(Bu^t,\ Et)$ based on the determination of the rate of formation of isobutane was unfortunately impossible. The separation between iso and n-butane on the chromatographic column was not sufficiently good. Small overlapping of the peaks did not affect the accurate determination of large amounts of n-butane, but introduced large uncertainty in the determination of small amounts of isobutane.

The ratio $k_3/(k_1 x k_6)^{\frac{1}{2}}$ deduced from some of the runs was found to be 1.9.

Isopropyl and t-butyl radicals. The reaction scheme in this case is

$$2\ C_3H_7 \longrightarrow C_6H_{14} \qquad 1$$
$$\longrightarrow C_3H_6 + C_3H_8 \qquad 2$$
$$C_3H_7 + t\text{-}C_4H_9 \longrightarrow C_7H_{16} \qquad 3$$
$$\longrightarrow C_3H_8 + iC_4H_8 \qquad 4$$
$$\longrightarrow C_3H_6 + iC_4H_{10} \qquad 5$$
$$2\ C_4H_9 \longrightarrow C_8H_{18} \qquad 6$$
$$\longrightarrow iC_4H_8 + iC_4H_{10} \qquad 7$$

Values deduced from the determination of the rates of formation of isobutene and propylene are respectively

$$\Delta(Pr^i,\ Bu^t) = 0.70$$

at pressures ranging from 11 to 15 mm Hg

$$\Delta(Bu^t,\ Pr^i) = 0.67$$

at pressures from 8 to 15 mm Hg.

The ratio of constants of disproportionation to combination of isopropyl radicals was taken as 0.63 [21].

The rate of formation of propane was also determined and a value $\Delta(Pr^i, Bu^t)$ = 0.68 found, in good agreement with the value deduced from the rate of formation of isobutene. The analytical system was not suitable for the accurate determination of small quantities of isobutane in the presence of large amounts of propylene, and $\Delta(Bu^t,\ Pr^i)$ could not be calculated using an equation similar to VII.

From the results of some of the runs, information on crosscombination of these radicals was gathered. The ratio $k_3/(k_1 x k_6)^{\frac{1}{2}}$ was found to be 2.02.

Notes on Tables 4.1, 4.2, and 4.3

All products are in rates of formation of 10^{12} mole cm^{-3} sec^{-1}, and all subsequent calculations involve these units.

A - Photolysis of trimethylacetaldehyde

a - Runs without reflector behind the lamp

a. f. - Analytical failure

b - Run carried out in the presence of 376 mm Hg of N_2

C - Rate of formation calculated. See text.

K - Photolysis of di-t-butyl ketone

P - Light filtered through a sheet of pyrex glass

DEK - Diethyl ketone
DIPK - Diisopropyl ketone
DTBK - Di-t-butyl ketone
} The figures in the Tables are mm Hg of pressure

C_2H_4 - Ethylene

C_2H_6 - Ethane

C_3H_6 - Propylene

C_3H_8 - Propane

$i\text{-}C_4H_8$ - Isobutene

$n\text{-}C_4H_{10}$ - n-Butane

C_6H_{14} (Table 4.2) - 2,2 dimethyl butane

C_6H_{14} (Table 4.3) - 2,3 dimethyl butane

C_7H_{16} - 2,2,3 trimethyl butane

C_8H_{18} - 2,2,3,3 tetramethyl butane

TABLE 4.1 DISPROPORTIONATION OF t-BUTYL RADICALS

RUN		t	T	P mmHg	$R_{i-C_4H_{10}}$	$R_{i-C_4H_8}$	$R_{C_8H_{18}}$	k_d/k_c (olefine)	k_d/k_c (parafine)
9	K	900	323.3	3.2	44.25	40.80	14.50	2.813	3.052
10	K	900	345.5	3.1	a.f	41.01	13.07	3.137	-
11	K	900	350.3	2.4	27.71	27.31	8.537	3.199	3.245
12	K	900	349.8	2.6	27.04	28.12	9.283	3.029	2.919
15	K	900	349.2	2.6	27.04	27.04	7.997	3.382	3.382
17	K	240	350.0	12.6	213.4	203.2	72.93	2.787	2.927
19	K	900	351.1	5.4	a.f	52.18	16.66	3.130	-
58a	K;P	3600	351.7	5.2	2.947	3.066	1.016	3.016	2.899
60	K;P	10800	350.3	4.9	2.055	1.972	.6155	3.211	3.339
63a	K;P	21660	351.3	5.2	2.768	2.650	.7846	3.375	3.526
47	A	900	353.0	11.9	-	20.87	6.369	3.277	-
64a	A	1800	347.9	33.7	-	15.65	5.014	3.121	-
66a	A	1800	347.8	32.0	-	27.81	8.333	3.337	-
67a	A	900	346.8	49.5	-	50.76	15.11	3.359	-
68a	A	900	346.4	52.5	-	53.26	15.99	3.331	-

TABLE 4. 2 PHOTOLYSIS OF DIETHYL KETONE/di-t-BUTYL KETONE MIXTURES

RUN	T°K	t	DTEK	DEK	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{nC_4H_{10}}$	$R_{iC_4H_8}$	$R_{C_6H_{14}}$	$R_{C_8H_{18}}$	$\frac{k_{ab}}{(k_{aa} \cdot k_{bb})^{\frac{1}{2}}}$	(Et,Bu^t)	(Bu^t,Et)
14	350	900	3.8	14.9			156.5	46.48	62.55	6.234	2.002	.4264	
16	353.6	900	3.5	15.7			179.3	39.85	53.92	3.930	2.031	.5071	
21	349	900	5.2	39.2			384.2	50.28	72.85	4.784	1.707	.4810	
22	352.7	1080	3.6	15.2			129.6	33.99	44.94	3.987	1.977	.4736	
23	348.5	900	4.4	19.2			168.9	42.69	73.54	5.964	1.849	.4028	
24	349.8	900	3.3	24.0			216.4	39.85	56.31	C3.664	-	.5003	
25b	352.7	900	4.0	19.4			229.6	50.28	68.94	C5.181	-	.4897	
75a	346.8	900	2.8	19.3			120.5	18.22	26.96	C1.507	-	.4979	
77a	348.3	900	3.7	13.9			95.81	24.26	32.18	C2.693	-	.4884	
76a	346.3	900	3.6	22.5			129.0	19.79	26.63	C1.375	-	.5786	
27	347.2	1200	4.6	2.2	9.750	5.387	C3.562		15.81	17.53	-	.5832	.3070
28	350.3	600	5.0	2.2	9.145	6.301	3.256		17.58	23.07	2.032	.4925	.3308
29	349.7	720	6.7	5.6	a.f	17.45	23.13		44.64	24.65	1.869	-	.3139
30	346.2	480	13.4	2.7	9.275	5.210	C .88		16.01	72.54	-	.5710	.3246
31	349.0	480	13.0	3.1	16.75	9.958	C5.481		36.72	60.98	-	.4338	.2488
33	354.4	480	11.3	2.0	5.971	3.355	C .526		10.68	54.13	-	.5521	.3069
36	352.5	480	10.2	2.7	10.29	5.464	C1.579		17.92	50.83	-	.5610	.2918

TABLE 4. 3 PHOTOLYSIS OF DIISOPROPYL KETONE/di-t-BUTYL KETONE MIXTURES

RUN	T°K	t	DTBK	DIPK	$R_{C_3H_6}$	$R_{C_3H_8}$	$R_{iC_4H_8}$	$R_{C_6H_{14}}$	$R_{C_7H_{16}}$	$R_{C_8H_{18}}$	$\frac{k_{ab}}{(k_{aa}xk_{bb})^{\frac{1}{2}}}$	(Pr^i, Bu^t)	(Bu^t, Pr^i)
38	355.3	480	3.	9.1			37.10	90.35	37.99	C 3.994	-	.6418	
39	353.1	480	2.1	12.1			26.94	124.9	29.61	C 1.754	-	.7194	
40	351.0	360	2.0	10.8			27.96	101.3	30.49	C 2.295	-	.6810	
44	352.8	480	1.3	10.3			15.75	111.5	18.30	C .7502	-	.7304	
46	352.7	900	1.9	9.1			19.11	80.09	20.87	C 1.363	-	.7076	
48	352.7	300	2.0	9.1			27.04	115.4	30.70	C 2.04	-	.6697	
87	347.7	480	2.0	13.0			12.07	93.65	14.23	C .54	-	.7273	
89	345.1	1500	2.2	12.3			6.465	63.74	7.685	C .2316	-	.7452	
90	344.5	900	2.0	11.2			9.014	71.36	10.84	C .412	-	.7106	
42	352.0	360	12.8	2.3	12.87	13.72		1.253	18.12	58.46	2.117	.7134	.6664
52	350.2	360	7.1	1.2	7.114	a.f		C .9452	9.995	26.42	-	a.f.	.6522
55	351.6	360	6.0	2.0	16.09	16.60		5.420	20.16	18.12	2.033	.6545	.6291
65	348.5	360	7.1	3.3	27.10	26.77		13.89	27.45	13.39	2.013	.6567	.6688
79	346.8	360	7.5	1.2	4.912	5.335		C .732	7.285	18.12	-	.6691	.6110
83	345.8	480	8.5	1.3	6.226	6.735		C .978	8.132	16.90	-	.7523	.6898
84	347.3	480	6.9	2.6	9.147	9.401		2.160	10.68	16.27	1.801	.7536	.7297
86	346.9	480	8.5	2.0	10.16	8.894		1.905	13.08	19.82	2.129	.5879	.6847

CHAPTER V

DISCUSSION OF RESULTS

5. 1 ADDITION REACTIONS OF ALKYL RADICALS TO ACETYLENE. The only attempt to measure the rate constant of addition of an alkyl radical to acetylene in the gas phase which can be regarded as sufficiently based on product analysis is that of Mandelcorn and Steacie [124] who used the material balance method. Their value for the rate of addition of methyl radical to acetylene is given by

$$k_3 = 10^{11.0}\ e^{-(5\,500/RT)}\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

The method employed in the calculation of results is likely to err, if at all, in yielding a high value for k_3. Their value of $\log k_3 = 8.1$ at 142°C is slightly higher than most values of rates of addition to unsaturated compounds at that temperature.

The value reported in the present work seems more reliable. Gas chromatography is a more satisfactory way of carrying out analysis of light hydrocarbons than mass spectrometry. Besides, results were calculated here by direct determination of the products concerned.

The rate constants for the addition of other radicals to acetylene have not been previously reported. The present values at 142°C fall into line with other rates of addition to unsaturated compounds at the same temperature. If in the calculation of the t-butyl results a value of 4.38 for the ratio of rate constants of disproportionation to combination is used [28], then the rate constant is given by

$$k_3 = 10^{10.7}\ e^{-(5\,300/RT)}\ \text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$$

5. 2 THE ISOMERIZATION OF ALKENYL RADICALS. Isomerization of alkyl radicals larger than butyl in the gas phase has been suggested in the past [9,39,126,127,128,130], in which a hydrogen atom would have been shifted from one carbon atom to another. The present example of isomerization cannot be explained in the same way. It might be explained by either a methylene insertion between two carbon atoms, or by a vinyl group migration. Preliminary results on the addition of n-propyl and isobutyl radicals to acetylene show the presence of 3,methyl butene-1 and 3,3 dimethyl butene-1 respectively in the products; they can only be explained by the shift of the vinyl group.

If the free energies of formation of the alkenyl radicals follow those of the hydrocarbons with an additional hydrogen atom the more highly branched radical is rather more stable than the isomer that is formed. The addition of an alkyl radical to acetylene is about 30 kcal.mole^{-1} exothermic; this energy is apparently sufficient to overcome the barriers to isomerization if it is not removed by collision. As the ratio acetylene/aldehyde seems to have little effect on the extent of the isomerization we may suppose that an activated unreactive complex is first formed in the addition process:

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad CH\cdot \\ \diagup \\ CH_3 \end{matrix} + CH{\equiv}CH \longrightarrow A^*$$

This complex A^*, if left undisturbed, will isomerize to give the radical with higher free energy of formation

$$A^* \longrightarrow CH_3CH_2CH_2CH{=}CH\cdot$$

A sufficiently high pressure in the system will deactivate the intermediate

before it has time to isomerize. There is no tendency at the lowest pressures to form an equilibrium mixture with the more highly branched olefin in slight excess.

We might then be tempted to write the following reaction scheme:

$$A^* + M \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\diagdown\!\!\diagup CHCH{=}CH + M \qquad 1$$

$$A^* \longrightarrow CH_3CH_2CH_2CH{=}CH \qquad 2$$

If both reactions are followed by the abstraction of a hydrogen atom from the aldehyde, we may write

$$R_{3,\text{methyl butene-1}} = k_1 [A^*] [M]$$

$$R_{\text{pentene-1}} = k_2 [A^*]$$

and

$$\frac{R_{\text{pentene-1}}}{R_{\text{3 methyl butene-1}}} = \frac{k_2}{k_1} \frac{1}{[M]}$$

When the ratio of isomers is plotted against the reciprocal of the pressure straight lines passing through the origin are obtained as shown in fig.5.1. The points correspond to experiments carried out at about 410°K.

The ratio of the rate of isomerization to that of deactivation for the addition of isopropyl radicals to acetylene is k_2/k_1 = 0.03 atm. and for addition of t-butyl radicals k_2/k_1 = 0.018 atm.

The formation of the additional olefins from both isopropyl and t-butyl radicals is the first definite evidence for the isomerization of small hydrocarbon radicals about which there has been considerable discussion.

5. 3 THE DISPROPORTIONATION OF t-BUTYL RADICALS. The ratio of rates of disproportionation and combination of t-butyl radicals have been found by Kraus and Calvert [22] to be 4.59 in a system in which di-t-butyl ketone was used as radical source. Photolysis of pivalaldehyde [28] gave 4.38, in good agreement with the previous determination. Boddy and Robb [105] obtained a value of 2.2 for the same ratio in a system in which radicals were generated by the mercury photosensitized hydrogenation of isobutene. Reasons for questioning the reliability of the last value have been advanced in an earlier chapter.

An examination of table 4.1 shows good reproducibility of the results there presented. One might be inclined to think that the present value is too low due to some error in chromatographic calibrations, if the above values are to be accepted. Underestimation of isobutane and isobutene is not likely as they are volatile hydrocarbons which can be easily condensed at liquid nitrogen temperature. Besides the calibration could be checked by comparison with similar calibrations carried out on the same apparatus by other workers in this laboratory. Calibration of octane was made directly by the method explained in chapter two which gave good results with other hydrocarbons. A check on the experimental technique was made by photolysing di-iso-propyl ketone; using the same set of calibrations employed throughout the work, a value of 0.61 was found for $\Delta(Pr^i, Pr^i)$ from the results of four runs, in good agreement with other published results.

One feels then the value of $\Delta(Bu^t, Bu^t) = 3.2$ to be real.

We may now examine the possibility of an underestimation of octane in the calibrations of Kraus and Birrell's. The calibration of octane in Birrell and Trotman-Dickenson's work was made by weighing mixtures of 2,3 dimethyl butane with octane; a drop of the mixture was then introduced into the gas chromatography apparatus and analysed. Use of the calibration curve for hexane permited the calculation of amounts of octane [131]. The vapour pressure of 2,3 dimethyl butane at 0°C is 100mm Hg. Evaporation from the mixture would lead to high values of $\Delta(Bu^t, Bu^t)$.

Nothing is said in Kraus and Calvert's paper about calibration, but it is likely that octane was underestimated. The values for the disproportionation ratios of isobutyl and sec-butyl radicals seem higher than other published results for the same radicals. It is probable that the high value for isobutyl is due to an unsufficient allowance for isobutene formed in the chain decomposition of the ketone source [30], but very likely this is not the only reason.

The fact that all three values seem high favours the belief in an underestimation of octane in the chromatographic calibrations previous to analysis.

5. 4 THE CROSSDISPROPORTIONATIONS OF t-BUTYL RADICALS WITH ETHYL AND ISOPROPYL

Values for the crossdisproportionation ratios in systems in which t-butyl radicals are mixed with either ethyl or isopropyl radicals have been reported [105]. The radicals were produced by the photosensitized hydrogenation of olefins. The reliability of the present study is based on the reproducibility of the results as may be seen from tables 4.2 and 4.3, and on the experimental technique used.

All runs have been carried out at approximately the same temperature. The

only example reported in which the ratio of rate constants seems to vary with temperature is that of n-butyl radicals[39]. This variation may be explained if we suppose that attack of a radical on the alkyl group of the aldehyde may take place at some extent at low temperatures. We have found that the olefin produced by this type of reaction may amount to as much as 60% at 200°C in the case of pivalaldehyde (see Chapter III of this thesis). In the latter case the attack will necessarily lead to the formation of isobutene. In the former, only part of it will produce butene-1. The rest might well explain the supposed isomerization of n-butyl radicals assumed by the authors [127].

An interesting problem in disproportionation reactions is the nature of the activated complex. By photolysis of partly deuterated diethyl ketone [94,95] the disproportionation of CH_3CD_2 was studied. Product analysis revealed all ethylene to be CH_2CD_2, hence a head-to-tail mechanism was suggested:

$$CH_3CD_2 \cdots H \cdots CH_2CD_2$$

It has been pointed out that the high A factors found for combinations of radicals could only be explained if complete freedom of the two part radicals is assumed in the activated complex. The A factors in disproportionation reactions are about the same size, and it is necessary to suppose that the two radicals enjoy much the same freedom of movement. This is not easily reconciled with the head-to-tail structure. It seems more likely that the dimer is first formed [48,132] (the A factor would be that normal for combination) and then decomposes by a four-centre reaction:

$$\begin{array}{l} CH_2 \cdots\cdots H \\ \quad | \qquad\quad \vdots \\ CD_2 \cdots\cdots CD_2CH_3 \end{array} \longrightarrow CH_2CD_2 + CH_3CD_2H$$

The activation energy for this decomposition would be provided by the high exothermicity of the dimerization. Accordingly a high pressure in the system would deactivate the complex and lead to low values of Δ(alk', alk''). It has been reported that disproportionations of alkyl radicals do not occur in the liquid phase[133]. This is not, however, quite clear[134]. On the other hand a radical which has an excess of energy from the process of its formation yields abnormally high values Δ[34], which are understandable on the same terms. Run 25 in table 4.2 was carried out in the presence of 376 mm Hg of nitrogen. This amount proved sufficient to deactivate the alkenyl radical formed when isopropyl radicals add to acetylene. No significant variation of the value of Δ(Et, Bu^t) was observed thus indicating that the radicals here produced are thermally equilibrated with their environment.

The mechanism might be tested[48] by investigating the crossdisproportionation of CH_3CD_2 and $CH_3CH_2CD_2$. The head-to-tail complex would give only CH_2CD_2 and CH_3CHCD_2. The presence of CH_3CDCD_2 in the products would indicate the formation of the dimer before disproportionation. Besides, the study of the influence of pressure on the extent of disproportionation should be extended to higher pressures in systems in which radicals are believed to be produced in thermal equilibrium with their environment.

It has often been suggested that the value of $\Delta$is in some way related to the number of hydrogen atoms whose abstraction would lead directly to the formation of a stable olefin. Ausloos and Steacie[79] found that a semiquantitative prediction of the rate constants for the disproportionation of n and isopropyl radicals was possible if their rates of combination were assumed to be equal. Kraus and Calvert[22] later found a relation between and the number of hydrogen

atoms available in each of the butyl radicals. Their conclusions seem however to be based on results which have been corrected by later publications [30,(b)]. Kerr and Trotman-Dickenson [48] plotted the recomended values of log (Alk',Alk'')/|H| where |H| is the number of H atoms whose removel from Alk'' would lead to formation of olefin. The pattern of results was marked, and permited prediction of values for other crossdisproportionations. The value $\Delta(Bu^t, Et)$ found in the present work agrees with the expected value. Other values do not agree at all. Their plot was based on a value of $\Delta(Me, Pr^i)$ which has been corrected later[125]. Bradley has suggested that if the mechanism in which disproportionation takes place via dimerization is correct, then it is probable that the relative probabilities of recombination and disproportionation are asociated with the stabilities of the various products. He compared values of Δ and $\Delta/|H|$ with the functions $(G^\circ_{dis} - G^\circ_{comb})/T$ and $S_{dis} - S_{comb}$ for a number of radicals. The latter functions represents the high-temperature limit of the former: as the intermediate in the reaction is highly activated, to an extent which depends on the exothermicity, better correlation with entropy function would be anticipated. Although the divergence becomes more marked with large radicals, predictions of the value of Δ for other reactions of ethyl radicals are possible using the value of $S_{dis} - S_{comb}$.

It seems that our present knowledge on disproportionation ratios is unsufficient and more reliable results must be obtained before any conclusion about the nature of the activated complex can be advanced.

5. 5 THE CROSSCOMBINATION OF t-BUTYL WITH ETHYL AND ISOPROPYL RADICALS. The values of 1.9 and 2.0 found for the ratio $k_{ab}^{\frac{1}{2}}/k_{bb}^{\frac{1}{2}}$ are in good agreement with similar ratios which can be found in the literature. They serve as a further

check of the experimental technique and the reliability of the analytical results. If we were to admit that the octane was overestimated and that the results of the analysis have to be multiplied by 3.2/4.5, the experimental ratios $k_{ab}/k_{aa}^{\frac{1}{2}} k_{bb}^{\frac{1}{2}}$ would then become 2.3 and 2.4 for t-butyl/ethyl and t-butyl/isopropyl respectively, which are higher than those for most alkyl radicals and thus, improbable.

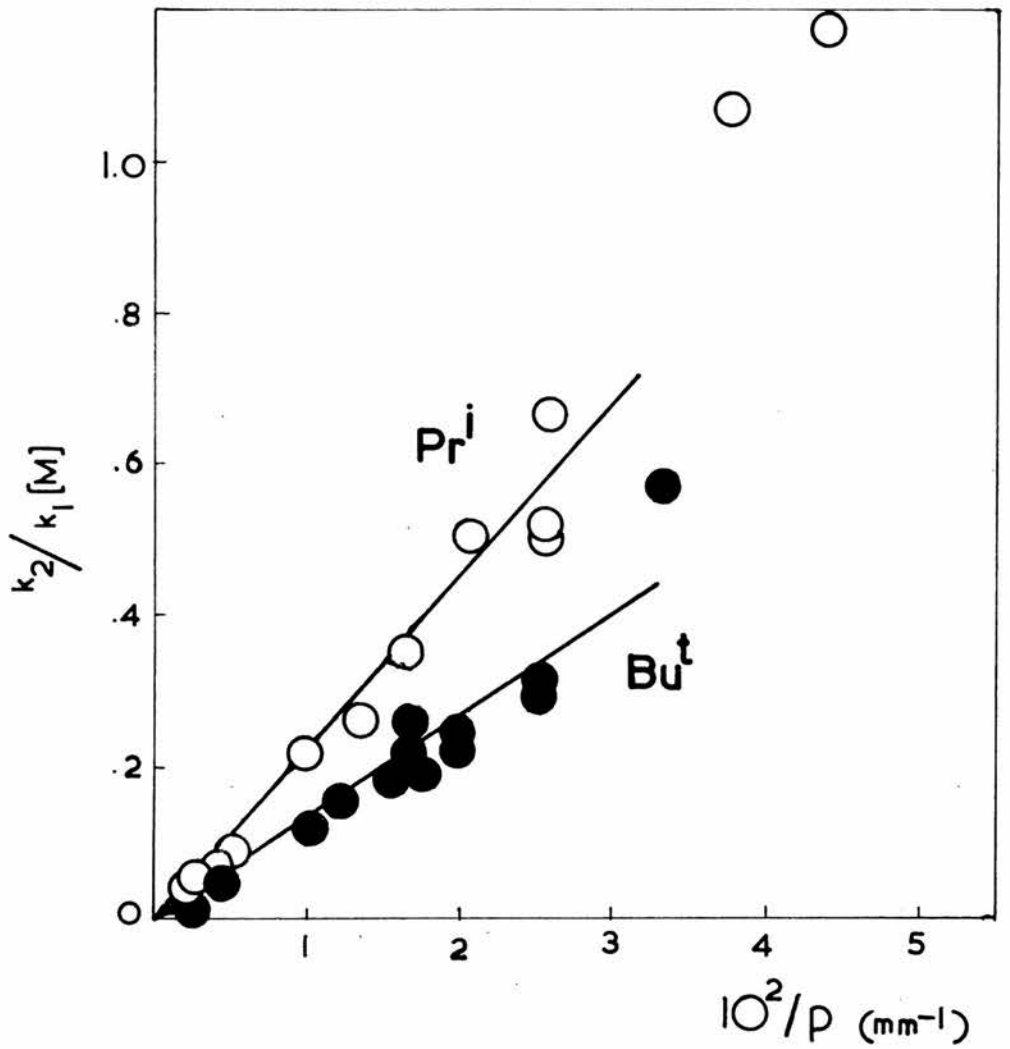


FIG. 5-1. Relative rates of isomerization and deactivation of alkenyl radicals as a function of pressure.

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